ELECTRICAL CONDUCTIVITY OF FLAMES

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Introduction

THIS article deals mainly with the electrical conductivity of ordinary Bunsen gas flames. Such flames are obtained by burning a mixture of coal or natural gas and air, usually with sufficient air to make the flame as hot as possible and so more than enough to make it "non-luminous." The flame formed by burning such a mixture, as it comes out of an ordinary burner, has fairly well-defined bounding surfaces consisting of the "inner cone" *ABC* and the "outer cone" *ADEFC* shown in Figure 1. The mixture of gases flows through the flame with an upward velocity of about 250 cm per second. The temperature just above the inner cone is about 2000°K, and near the top of the flame about 1900°K. The gases in the flame above the inner cone are mainly nitrogen, steam, carbon monoxide, and carbon dioxide. The carbon monoxide burns to dioxide near the outer cone.

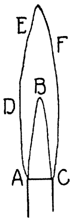

Fig. 1. Bunsen flame.

The electrical conductivity of the flame can be studied by putting two platinum electrodes in it and measuring the current due to a potential difference. The current can be greatly increased by the addition of alkali metal salt vapors to the flame.

The conductivity is supposed to be due to the presence of positive and negative ions as in other cases of gaseous conductivity.

The results obtained by different experimenters on the electrical properties of flames frequently differ very considerably. Such differences are due largely to differences between the flames and to apparently unimportant differences in the experimental methods used. During the preparation of this article several series of experiments have been carried out with the object of clearing up such discrepancies.

References to some of the original sources are given below. References to the others may be found in "Die Elektrischen Eigenschaften der Flamme" by A. Becker, Leipzig, 1929. (Wien-Harms Handbuch der Experimental Physik.) It is not proposed in this article to give any account of the earlier work on the subject. Only the more recent experiments are described.

1. Relation Between Current, Potential and Distance Between Electrodes in a Bunsen Flame

A convenient apparatus for studying the conductivity of a Bunsen flame is shown in Figure 2. The burner *BB* is a fused quartz tube about 3 cm in diameter and 30 cm long, with a slot about 2 mm wide and 15 cm long cut parallel to the axis of the tube. One end of the tube is closed with a cork and the other is connected by means of a rubber tube to a sprayer *S*. Air at 15 to 30 cm of mercury above atmospheric pressure is passed into the sprayer through the glass tube *T* which is drawn out to a nozzle about 1.5 mm in diameter as shown. Coal or natural gas enters the sprayer through the tube *G* the end of which should be near to the air nozzle so that the gas and air may be thoroughly mixed together. The mixture is burned at the slot in the quartz tube and its composition can be adjusted by varying the gas and air pressure so as to give a uniform flame about 8 cm high with a sharply defined inner cone about one cm high. When it is desired to add a salt vapor to the flame a solution of the salt is put into the sprayer and a small tube is attached to the nozzle, as shown, up which the solution is sucked and sprayed into the mixture of gas and air. In this way the flame can be uniformly filled with the salt vapor. The amount of the salt vapor can be varied by changing the concentration of the solution sprayed. The conductivity of the flame can be studied by means of two platinum electrodes *EE* which may be connected to a battery and galvanometer. The electrodes may be pieces of sheet platinum about 3 by 1 cm supported on platinum wires.

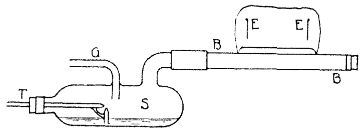

Fig. 2. Apparatus for studying conductivity of Bunsen flame.

The relation between the current (c), the potential difference (P) between the electrodes and the horizontal distance (d) between the electrodes, when the electrodes are both completely immersed in the flame and equally hot, is found to be given approximately by the equation

$$P = Acd + Bc^2$$

where A and B are constants for a given flame. With P in volts, c in amperes and d in cm the constant B is about 10^{14} and A about 10^6 for a flame like that described when free from metal vapor.

Thus for example, with $d = 10$ cm we get the data of Table I.

If a solution of an alkali metal salt, such as potassium carbonate, is sprayed into the flame, the currents are greatly increased. The relation between P, c and d remains approximately $P = Acd + Bc^2$ but the constants A and B depend on the nature and amount of the salt vapor sprayed into the flame.

The variation of the potential between the electrodes can be examined by means of a probe wire put in the flame. The potential difference between the probe and one of the electrodes can be measured with a well-insulated quadrant electrometer or electrostatic voltmeter. It is found that usually there is a nearly uniform potential gradient in the flame except quite near to the electrodes. Near the negative electrode the gradient increases and becomes very large close to it. There is usually a drop in the potential near the negative electrode which is a large fraction of the potential difference between the electrodes. In the equation $P=Acd+Bc^2$ the term Bc^2 represents the drop near the cathode and Acd the fall of potential in the uniform gradient. The uniform gradient is found to be nearly proportional to the current. If the cross section of the flame perpendicular to the direction of the current is a square cm then Aa is equal to the specific resistance of the flame. Aa is usually of the order of a million ohms per cm^3 for a pure Bunsen flame adjusted so as to be as hot as possible.

TABLE I. *Sample data illustrating that* $P=Acd+Bc^2$.

c (amperes)	Acd (volts)	Bc^2 (volts)	P (volts)
10^{-7}	1	1	2
5×10^{-7}	5	25	30
10^{-6}	10	100	110
3×10^{-6}	30	900	930

If the cathode is coated with lime or barium oxide the potential drop at it is greatly reduced and may completely disappear provided the current passed through the flame is not too large. The current is then given roughly by $P=Acd$, and so is greatly increased by the oxide on the cathode.

The above experimental results may be explained by means of the ionic theory of gaseous conductivity if we suppose that the flame gases contain a large number of positive and negative ions and that the mobility of the negative ions is much greater than that of the positive ions. The following theory is a slightly modified form of that due to J. J. Thomson.[1]

Let n_1 and n_2 denote the numbers of positive and negative ions per cc and e the positive ionic charge so that $(n_1-n_2)e$ is the charge per cc. Then if F denotes the electric field strength and x the distance from the positive electrode we have $dF/dx=4\pi e(n_1-n_2)$. Hence in the uniform potential gradient where $dF/dx=0$ we must have $n_1=n_2$.

If v_1 and v_2 denote the velocities of the ions due to the electric field then we may put $v_1=k_1F$ and $v_2=k_2F$ where k_1 and k_2 are the ionic mobilities. The mobility k_1 of the positive ions is probably independent of F but k_2 that of the negative ions probably decreases to some extent as F increases. The current density i in the uniform gradient (F_0) is then given by

$$i = neF_0(k_1 + k_2)$$

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[1] Conduction of Electricity through Gases.

where $n = n_1 = n_2$. If the cross section of the flame is a then the current c is equal to ia so that $c = aneF_0(k_1 + k_2)$. The term Acd in the equation $P = Acd + Bc^2$ is equal to F_0d so that $c = F_0/A$ and therefore $A = 1/ane(k_1 + k_2)$. The specific resistance of the flame is equal to $1/ne(k_1 + k_2)$.

We have $e = 4.8 \times 10^{-10}$e.s.u. or 1.6×10^{-19} coulombs and k_2 is believed to be about 2500 cm/sec. for one volt/cm so that since k_1/k_2 is small and $r = 10^6$ ohms/cm^3 we get $10^{-6} = n \times 1.6 \times 10^{-19} \times 2500$ which gives $n = 2.5 \times 10^9$. Thus in a pure Bunsen flame the number of ions per cc is about $2.5 \times 10.^9$ If an alkali salt is sprayed into the flame the number of ions per cc may be increased to 10^{11} or more. At 2000°K and atmospheric pressure a gas contains about 4×10^{18} molecules per cc so that the number of molecules in the pure flame is about 2×10^9 times greater than the number of positive or negative ions.

The ionization in the flame is believed to be due to the emission of electrons by the neutral atoms or molecules present. For example, potassium atoms in the flame are believed to dissociate into electrons and positively charged potassium atoms in accordance with the equation

$$K \rightleftarrows K_+ + e$$

where e denotes an electron. The nature of the substance or substances which give rise to the ions in a pure flame is not known. It is difficult to obtain a flame entirely free from traces of sodium but it seems probable that a Bunsen flame containing no sodium or other metals has about 10^9 ions per cc in it. Spraying ordinary distilled water into the flame usually increases its conductivity several times but water distilled and stored in fused quartz vessels and sprayed in a fused quartz sprayer has little or no effect on the conductivity.

If q denotes the number of electrons produced per cc per second then in the uniform potential gradient in the flame where as many ions enter any region as leave it we have $q = \alpha n^2$ where α is the coefficient of recombination and $n = n_1 = n_2$ as before. The cathode and anode are surrounded on all sides by fairly well-defined layers or sheaths in which the electric field increases rapidly as the surface of the electrode is approached.

In these sheaths the ionization is greater than the recombination and provided the emission of negative ions by the cathode can be neglected the difference is equal to the number of negative ions which flow per second from the cathode to the anode through the uniform gradient where the ionization and recombination are equal. At a plane cathode if F_0 denotes the field strength in the uniform gradient we have

$$nk_2F_0 = \int_0^{l_2} (q - \alpha n_1 n_2) dx$$

where l_2 is the thickness of the sheath and x the distance from the cathode surface. At the surface of the cathode, provided it does not emit an appreciable number of electrons, we have $n_2 = 0$ so that $q - \alpha n_1 n_2 = q$ and at the surface of the sheath where $x = l_2$ we have $q - \alpha n_1 n_2 = 0$. The way in which

$q-\alpha n_1 n_2$ varies between $x=0$ and $x=l_2$ is not known but it is clear that any possible variation may be approximately represented by the equation

$$q - \alpha n_1 n_2 = q(1 - x/l_2)^m$$

where m is a constant.[2] Assuming this value we get $nk_2F_0=ql_2/(m+1)$. With the equation

$$i = neF_0(k_1 + k_2)$$

this gives $i=qel_2(k_1+k_2)/k_2(m+1)$. If l_1 denotes the thickness of the layer or sheath on the positive electrode then in the same way we get $i=qel_1(k_1+k_2)/k_1(m+1)$ so that $l_1/l_2=k_1/k_2$. It is found that l_1/l_2 is a small fraction so that k_1 must be small compared with k_2. k_1+k_2 is therefore nearly equal to k_2 so that $i=qel_2/(m+1)$. The thickness of the cathode sheath should therefore be proportional to the current density.

The number of electrons flowing through one cm^2 per second is equal to n_2k_2F so that if x denotes the distance from the cathode

$$\frac{d}{dx}(k_2n_2F) = q - \alpha n_1 n_2 \tag{1}$$

and in the same way for the positive ions

$$-\frac{d}{dx}(k_1n_1F) = q - \alpha n_1 n_2. \tag{2}$$

Multiplying the equation $-dF/dx=4\pi e(n_1-n_2)$ by F and differentiating it with respect to x we get

$$\frac{d}{dx}\left(F\frac{dF}{dx}\right) = 4\pi e\left(\frac{d}{dx}(n_2F) - \frac{d}{dx}(n_1F)\right)$$

so that if we assume k_1 and k_2 to be constants we have using (1) and (2)

$$\frac{d^2F^2}{dx^2} = 8\pi e\left(\frac{1}{k_1} + \frac{1}{k_2}\right)(q - \alpha n_1 n_2).$$

Putting

$$q - \alpha n_1 n_2 = q(1 - x/l_2)^m$$

and

$$q = \frac{ik_2(m+1)}{el_2(k_1 + k_2)}$$

this gives

$$\frac{d^2F^2}{dx^2} = \frac{8\pi i(m+1)}{k_1l_2}\left(1 - \frac{x}{l_2}\right)^m$$

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[2] J. J. Thomson took $q-\alpha n_1n_2=q$ which corresponds to $m=0$.

Integrating twice and putting $dF^2/dx = 0$ and $F = F_0$ at $x = l_2$ we get

$$F^2 - F_0^2 = 8\pi i l_2 (1 - x/l_2)^{m+2}/(m + 2)k_1.$$

In most cases F_0^2 is small compared with F^2 so that we have approximately for the cathode fall of potential P_2 which is equal to $-\int_0^{l_2} F dx$

$$P_2 = \left(\frac{8\pi i l_2}{k_1(m + 2)}\right)^{1/2} \int_0^{l_2} \left(1 - \frac{x}{l_2}\right)^{(m+2)/2} dx$$

which gives

$$P_2 = \left(\frac{8\pi i l_2^3}{k_1(m + 2)}\right)^{1/2} \frac{2}{m + 4}.$$

Since $l_2 = i(m+1)/qe$ it follows that

$$P_2 = \frac{2}{m + 4}\, i^2 \left(\frac{8\pi(m + 1)^3}{k_1 q^3 e^3 (m + 2)}\right)^{1/2}.$$

The difference of potential between the electrodes P is therefore given approximately by the equation

$$P = \frac{d\alpha^{1/2} i}{(k_1 + k_2) e q^{1/2}} + \frac{2}{m + 4}\left(\frac{8\pi(m + 1)^3}{k_1 q^3 e^3 (m + 2)}\right)^{1/2} i^2$$

since the potential drop at the anode is very small. This agrees with the empirical equation $P = Adc + Bc^2$.

If the cathode emits an appreciable number of electrons the equation

$$nk_2 F_0 = \int_0^{l_2} (q - \alpha n_1 n_2) dx$$

requires modification. Let the number of electrons emitted per cm^2 per sec. be N then we have

$$nk_2 F_0 = N + \int_0^{l_2} (q - \alpha n_1 n_2) dx.$$

If $nk_2 F_0 = N$ the integral is zero and there is no drop of potential at the cathode. The uniform gradient then extends right up to the cathode. When the cathode is coated with lime or baryta N becomes large and the cathode fall of potential disappears unless the current density is greater than Ne.

The cathode sheath has been carefully studied recently by P. E. Boucher[3] and by H. E. Banta.[4]

Banta used a plane cathode consisting of a circular disk of platinum surrounded by a guard ring and so was able to determine the current density at the disk accurately. The variation of the potential near the disk was examined by means of an insulated probe wire and so the thickness of the sheath was determined.

[3] Boucher, Phys. Rev. **31**, 833 (1928).

[4] Banta, Phys. Rev. Feb. (1929).

Banta obtained the results shown in Table II with a flame, the conductivity of which was increased by spraying a solution of four grams of potassium chloride, in a liter of water into it.

TABLE II. *Banta's results for the conductivity of a flame into which a solution of KCl was sprayed.*

l_2 (cm)	P_2 (volts)	$i\times10^6$ (amperes)	$10^{12}il_2^3/P_2^2$
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

It appears that il_2^3/P_2^2 does not vary much. It is difficult to measure the thickness of the sheath accurately and the variations in il_2^3/P_2^2 may be due entirely to errors in the values of l_2. For example if we take l_2 equal to 0.14 instead of 0.13 we get $10^{12}il_2^3/P_2^2$ equal to 5.68 instead of 4.54.

With KCl solutions of different concentrations Banta obtained the results shown in Table III.

TABLE III. *Variation of flame conductivity with concentration of salt solution* (*Banta*).

KCl gm/liter	l_2 (cm)	P_2 (volts)	$i\times10^6$ (amperes)	$10^{12}il_2^3/P_2^2$
0	0.87	132	0.146	5.52
1/16	0.425	139	1.35	5.36
1/4	0.33	130.5	2.70	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

When spraying a solution of caesium chloride and one of rubidium chloride he found the following values:

	l_2	P_2	$i\times10^6$	$10^{12}il_2^3/P_2^2$
CsC*l*	0.22	138	10	5.59
RbC*l*	0.265	139	5.2	5.08

According to the theory il_2^3/P_2^2 is equal to $k_1(m+2)(m+4)^2/32\pi$ and so should be constant so long as k_1 the mobility of the positive ions is the same. Banta's results therefore indicate that the positive ions of potassium, rubidium and caesium and of the pure flame all have nearly the same mobility. The value of k_1 is believed to be about 2 cm/sec. for one volt/cm. Banta's value of il_2^3/P_2^2 makes k_1 equal to about 2 if the constant m is taken equal to 4.

The equation $l_2=[i(m+1)]/qe$ with $m=4$ gives $qe=5i/l_2$. For the pure flame Banta found $i=0.146\times10^{-6}$ amperes and $l_2=0.87$ cm so that $qe=5\times0.146\times10^{-6}/0.87=8.4\times10^{-7}$ coulombs or 2520 e.s.u. This makes q equal to $2520/4.77\times10^{-10}$ or 5.30×10^{12}. The number of ions per cc in the pure flame as we have seen above is about 2.5×10^9 so that since $q=\alpha n^2$ where α is the coefficient of recombination we get $\alpha=q/n^2=5.3\times10^{12}/6.25\times10^{18}=8.5\times10^{-7}$. The coefficient of recombination of the ions produced in air at atmospheric pressure and at about 300°K by x-rays is equal to about 14 $\times 10^{-7}$. It is remarkable that the coefficient of recombination at 300°K should differ so little from that in a flame at about 2000°K.

The value of the mobility of the positive ions in a Bunsen flame has been estimated roughly[5] with the apparatus shown in Figure 3. A mixture of gas and air was burned from a burner *B* about 3 cm in diameter giving a flame *F*. The burner *B* was inside a brass tube which supported a horizontal grating of platinum wires about 2 cm above the top of the burner. A loop of platinum wires was placed at the center of the grating so that the grating formed a guard ring around it. The wire *W* supporting the loop was passed through a hole in the tube *T* and was connected to a galvanometer. The other terminal of the galvanometer was connected to the tube *TT*. The upper part of the flame entered a chimney *C* which carried away the flame gases. The lower end of this chimney supported a horizontal platinum wire grating across the upper part of the flame. The distances between the two gratings was 7 cm.

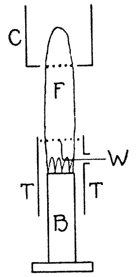

Fig. 3. Apparatus for estimating roughly the value of the mobility of the positive ions in a Bunsen flame.

When a potential difference was maintained between the chimney and the tube *TT* the galvanometer indicated a small current which passed along the axis of the flame to the loop of wire at the center of the lower grating. If a bead of salt on a platinum wire was put in the flame just below the upper grating the galvanometer current was not appreciably changed when the upper grating was at the higher potential with potential differences up to about 3000 volts. With 3000 volts the potential gradient in the flame near the upper grating was about 100 volts per cm and the velocity of the flame was 300 cm per sec. If positive ions from the salt vapor moved down the flame they would be deposited on the lower grating and metal vapor would accumulate there and increase the conductivity which would decrease the potential fall at the lower negative electrode and so increase the gradient higher up which would increase the current. Since the current was not increased it follows that the positive ions of the salt vapor did not move down the flame. The mobility of the positive ions must therefore be less than 3 cm per sec. for one volt per cm.

With the two gratings nearer together it was found that the current was increased by the salt bead when the potential gradient was about 300 volts per

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[5] H. A. Wilson, Phil. Trans. **A216**, 63 (1915).

cm. The mobility of the positive ions is therefore about one cm per sec. for one volt per cm. It could not be determined accurately because the increase in the current did not appear sharply at a definite gradient but increased slowly with the gradient. These experiments show that the mobility of the positive ions is not much greater than one cm per sec. for one volt per cm. It might be two or even three cm per sec. The mobility is about the same for any alkali metal. Andrade[6] found about 2.5 cm/sec. per volt/cm for the positive ions of strontium. Many earlier experiments now believed to be erroneous gave considerably higher values of k_1.

It appears that the mobility of the positive ions in flames at about 2000°K is not much different from that of the positive ions produced by x-rays in air at atmospheric pressure which is about 1.4 cm/sec. per volt/cm.

If a bead of a sodium salt on a platinum wire is put in the upper part of a Bunsen flame and a clean platinum wire in the lower part then if a potential difference of about ten thousand volts is maintained between the two wires with the upper one positive, sodium is deposited on the lower wire which is made evident by the yellow coloration of the flame close to it. No visible effect is produced with the upper wire negative. The sodium ions are deposited on the lower wire and then evaporate as sodium vapor which colors the flame. The yellow sodium light, of course, is produced by electrically neutral sodium atoms not by the positive ions.

Lenard found that the coloured streak of vapor from a salt bead in a flame could be deflected by an electric field. This deflection is probably largely due to the streak becoming positively charged by losing electrons so that the whole streak including the flame gases in it is deflected towards the negative electrode. A full account of this is given in A. Becker's book. The deflection observed indicates a velocity of about 0.05 cm/sec. for one volt/cm.

2. THE HALL EFFECT IN FLAMES

Since the mobility of the negative ions is much greater than that of the positive ions in flames we should expect a large Hall effect. E. Marx first measured the Hall effect in a Bunsen flame and it has since been investigated by H. A. Wilson, J. S. Watt, P. E. Boucher and C. H. Kean. These experimenters have obtained conflicting results but all agree that there is a large effect in the direction to be expected. It will be convenient to consider the theory of the effect first.

Let the flame from a slot in a quartz tube, as described above, be put in a horizontal magnetic field of strength H perpendicular to the plane of the flame and let a current be passed between two electrodes one near each end of the flame. Since the flame is insulated or nearly so, no appreciable current can escape from it so that the current must flow horizontally between the electrodes. That the current through the flame is very large compared with any current which can escape from it can be easily shown by moving one of the electrodes outside the flame. The current then becomes very small compared with the current when both electrodes are in the flame.

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[6] Dissertation, Heidelberg (1911).

In the central region of the flame away from the electrodes there is a uniform electric field which has a horizontal component and a vertical component due to the magnetic field. The vertical component is uniform in the central region not too near the top or bottom of the flame. With no magnetic field there is usually a vertical potential gradient but it is small compared with that due to a magnetic field of 1000 gauss. The flame gases move up with a velocity of about 250 cm per sec. The gases entering the flame at the bottom, of course, contain no ions so that at the bottom of the flame there is a layer in which there is an excess of ionization over recombination. Above this layer the flame is nearly uniform and the ionization and recombination are nearly equal. Near the top of the flame where the temperature begins to fall rapidly the ions disappear so that there is an excess of recombination. The layers at the top and bottom, in which the ionization and recombination are not equal, are analogous to the sheaths on the electrodes. Between the sheaths and the top and bottom layers there is a nearly uniform region in which the ionization and recombination are equal and the electric field is uniform. We shall consider the theory of the Hall effect in this uniform region.

It is important to note that the application of uniform electric and magnetic fields to such a uniform region does not disturb the uniformity but merely produces a flow of the ions across the region so that as many enter any element of volume as leave it. An intense field will cause an increase in the thickness of the bounding layers in which the ionization and recombination are unequal but so long as these layers do not extend over the whole area a uniform region in which ionization and recombination are equal will remain in the middle.

As is well known the Hall effect depends on the difference between the velocities of the positive and negative ions but since in flames the velocity of the negative ions is about a thousand times greater than that of the positive ions the difference is practically equal to the velocity of the negative ions. The theory of the Hall effect in salt solutions has frequently been supposed to be applicable to flames but this idea is erroneous. In a salt solution it is necessary that the transverse streams of both the positive and negative ions, due to the magnetic field, be zero because the ions cannot escape from the solution. It is therefore necessary to suppose that a transverse concentration gradient is set up which together with the transverse electric field reduces the transverse velocities of both kinds of ions to zero. The concentration gradient necessary for this in a flame would be very large and would be easily detected in the case of a flame containing sodium vapor by the altered distribution of sodium light in the flame. No such effect is observed and there is no reason to expect it in flames because the rapid upward stream of gases through the flame makes it impossible for any appreciable concentration gradient of positive ions to be set up. This is so because the velocity of the positive ions due to the vertical field is small compared with the velocity of the flame gases. The ions are continually produced at the bottom of the flame and disappear by recombination at the top and the neutral atoms formed pass out of the flame so that the condition which has to be satisfied is that the upward flow of positive ions must be equal to that of the negative ions so that the vertical current may be zero. In the uniform region the number of positive ions per cc is equal to that of the negative ions so that the upward velocity must be the same for both kinds of ions.

The force on a positive ion due to an electric field X is equal to Xe and this force causes the ions to move with a velocity k_1X so that the velocity of a positive ion due to unit force is $k_1X/eX = k_1/e$. In the same way the velocity of a negative ion due to unit force is k_2/e. The upward force on a positive ion in the flame is equal to $Ye - Hek_1X$ since the horizontal velocity is approximately k_1X so that the upward velocity of the positive ions is equal to $V + (k_1/e)\ (Ye - Hek_1X)$ where V is the upward velocity of the flame gases. In the same way the upward velocity of the negative ions is $V + (k_2/e)\ (-Ye - Hek_2X)$ so that we have

$$V + \frac{k_1}{e}(Ye - Hek_1X) = V + \frac{k_2}{e}(-Ye - Hek_2X)$$

or

$$Y(k_1 + k_2) = HX(k_1^2 - k_2^2)$$

which gives

$$k_1 - k_2 = Y/HX$$

or since k_1/k_2 is small $k_2 = -Y/HX$. The upward velocity of the ions is therefore very nearly equal to V.

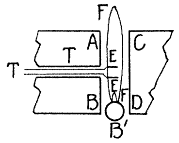

Fig. 4. Apparatus used in experiments on Hall effect in flames.

In the above we have neglected the horizontal force on the ions due to their vertical motion in the magnetic field. The upward velocity V is about 300 cm/sec. so that with a field of 5000 gauss the horizontal force is equivalent to a field of $300 \times 5000/10^8$ or 0.015 volt/cm which is quite negligible since the horizontal field is of the order of 10 volts/cm.

This theory depends on the assumption that all the electrons move horizontally with the velocity k_2X. This is not exactly true because k_2X is really only the average velocity of the electrons due to the field X. A more rigorous calculation similar to that due to Gans[7] for the Hall effect in metals, on the classical theory, gives $k_2 = -8Y/3\pi HX$. Since the experimental results on the Hall effect are subject to considerable error the factor $8/3\pi$ is unimportant and the simple theory given above quite adequate at present.

All the more recent experiments on the Hall effect in flames have been made with an apparatus similar to that shown in Figure 4. B' is a quartz tube burner with its slot perpendicular to the plane of the paper and FF is the

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[7] Ganz, Ann. d. Physik (4) **20**, 293 (1906).

flame seen end on. AB and CD are the poles of a large electromagnet one on either side of the flame. The pole AB has a hole in it about one cm in diameter in which a brass tube TT fits. This tube supports two platinum wires EE in the flame. These wires are parallel to the axis of the tube and lie in the same plane as the axis at equal distances on either side of it. The wires EE are well insulated by quartz tubes and are connected to a quadrant electrometer by wires coming out at the other end of the tube TT. The electrometer and the battery used to charge its needle must be well insulated from the ground. The tube TT carries a vernier by means of which any angle through which it is turned can be read on a graduated circle. A current is passed through the flame between two platinum electrodes about 12 cm apart placed on either side of the wires EE. The current is perpendicular to the plane of the figure. The tube TT is turned around until the electrometer indicates that the wires EE are at the same potential. With no magnetic field the plane containing the two wires should then be very nearly vertical. When a magnetic field is produced the electrometer is deflected and the deflection can be reduced to zero by rotating the tube TT through a small angle. If the magnetic field is reversed the rotation required to make the deflection zero is also reversed in direction and should be nearly equal to its previous value. The angles can be easily measured to one or two tenths of a degree. To obtain satisfactory results it is necessary that the flame be large enough for the wires EE to be well removed from the top and bottom of the flame and from the electrodes. The flame should be at least 10 cm high if the wires EE are between one and two cm apart. The wires EE should be in a uniform part of the flame. The negative electrode may be coated with lime or baryta so as to diminish the potential drop at it and so increase the current and the uniform gradient between the electrodes.

The angle θ through which the equipotential surfaces in the flame are rotated by the magnetic field is given by the equation $\tan \theta = F_y/F_x$ so that we have $\tan \theta = Hk_2$ since k_1/k_2 is small. Marx who first studied the Hall effect in flames found F_y to be nearly proportional to H and to F_x. This was confirmed by H. A. Wilson who found $\tan \theta$ to be nearly proportional to H and to be nearly independent of F_x. J. S. Watt and P. E. Boucher both found the angle θ to vary considerably with the horizontal electric field F_x. Watt found $k_2 = -Y/HX$ to vary regularly from 2640 cm/sec. per volt/cm for small values of X to 1600 with $X = 30$ volts/cm for a flame made highly conducting with potassium. For a pure flame it varied from 2660 with $X = 4$ volt/cm to about 2000 with $X = 30$. Boucher found k_2 to vary from 2900 with $X = 2$ to 2300 with $X = 38$ for a pure flame at about 2000°K. In cooler flames he found k_2 to decrease rapidly and then increase as X was increased. Marx found k_2 to decrease as the conductivity of the flame was increased by adding any alkali metal to it. H. A. Wilson, Watt and Boucher found k_2 to be nearly independent of the conductivity. Thus according to Marx and Wilson k_2 is nearly independent of X but according to Watt and Boucher this is not so and according to Marx k_2 decreases as the conductivity increases but according to Wilson, Watt and Boucher it remains nearly constant. In view of these conflicting results a series of experiments on the Hall effect has been made by C. H. Kean under my direction. The apparatus was similar to that already described.

To see if altering the conductivity changed the Hall effect angle the sprayer was arranged so that the nozzle could be rotated through a right angle so as to remove the sprayer tube from the solution. In this way the supply of salt solution spray could be quickly stopped and started without altering anything else. It was found that the Hall effect angle was practically the same with the sprayer working or not working. This was tried with strong solutions of potassium salts which greatly increased the conductivity and also with weaker solutions.

A great many experiments were made on the variation of the Hall effect with the horizontal electric field X. It was found that large variations may occur. Increasing the size of the flame diminished these variations considerably. With a large flame about 12 cm high and 15 cm long made highly conducting by spraying a potassium chloride solution the Hall effect angle was nearly independent of X. The following table contains one set of results showing this. The magnetic field strength was 3720 gauss in each case.

Potential difference between electrodes (volts)	90	135	180	45	225	270
Hall effect angle (degrees)	7.2	7.5	7.2	6.8	7.7	7.4

The field strength X was about equal to the P.D. divided by 12 and so was changed from 4 volts/cm to 22 volts/cm.

In a pure flame it was found that the Hall effect angle usually varied more or less with the horizontal electric field X.

In C. H. Kean's earlier experiments with pure flames the Hall effect usually decreased as X was increased. In the later experiments in which a larger flame was used it usually increased with X. Table IV contains all Kean's re-

TABLE IV. *Kean's results on the Hall effect in pure flames.*

P. D. (Volts)	$(\tan\theta/H)\times10^5$	Mean
45	2.93, 3.07, 2.89, 3.87, 3.78, 3.56, 3.33, 3.14, 3.23, 4.06	3.39
90	3.20, 3.59, 3.35, 3.96, 3.70, 3.03, 3.29, 3.72, 4.25	3.56
135	4.53, 4.25, 3.92, 3.57, 3.13, 3.75, 4.07, 3.37, 4.04, 3.84, 3.94, 4.24, 3.50, 3.80, 4.06	3.87
180	4.58, 4.17, 3.59, 3.23, 3.43, 3.72. 4.54, 3.18	3.80
225	4.67, 3.58, 3.72, 2.73, 2.31, 3.09, 4.75, 4.83, 4.26	3.77
270	4.80, 4.75, 2.92, 3.90, 5.02, 5.14, 4.50	4.43
315	5.57, 5.09, 3.92, 3.65	4.56
	Average	3.91

sults with the larger pure flame. Each number is a result of observations made, at a different time, usually on a different day. These results seem to indicate a definite increase of tan θ/H with the potential difference between the electrodes. However, the values obtained with each potential differ considerably so that the increase is rather doubtful. Thus the results obtained with a magnetic field equal to 5850 are as follows:

P.D. (volts)	45	90	135	180	225	270	315
(tan θ/H)$\times 10^5$	3.33	3.03	3.57	3.23	2.31	2.92	3.92
	3.14	3.29	3.13				

These results do not show any certain increase with the potential difference.

If the effect is independent of the electric field with a flame containing potassium and also equal for a pure flame and for a flame containing potassium then it should be independent of the field for a pure flame. Some experiments with a pure flame gave an increase with the electric field and some a decrease. Further experiments are required to find out the reason for these discrepancies but it seems probable that the results obtained with a highly conducting flame are more reliable than those obtained with a pure flame.

It is found that the current through the flame is proportional to the electric field strength. This seems to require that the ionic velocities should be proportional to the field strength and so that the Hall effect angle should be independent of the field strength.

I think therefore, that the variations of the Hall effect angle with the electric field strength are probably more apparent than real.

The Hall effect appears to have practically the same value in flames containing any alkali metal as in a pure flame. Thus the writer found practically equal values of tan θ/H for a pure flame and for one containing lithium, sodium, potassium, rubidium or caesium.

C. H. Kean found the following values of tan θ/H:

	(tan θ/H)$\times 10^5$	Mean
Pure flame	3.39 to 4.56	3.91
Potassium	3.86 3.44 3.97 4.27	3.88
Lithium	4.42 4.15	4.28

The following table contains the values of tan θ/H found by different observers:

	(tan θ/H)$\times 10^5$
H. A. Wilson	2.45
J. S. Watt	2.6*
P. E. Boucher	2.8*
C. H. Kean	3.9

The difference between these results may be attributed to differences between the flames.

The velocity of the negative ions due to one volt per cm is equal to (tan θ/H)10^8 so that it appears that k_2 varies from 2450 to 3900 cm/sec. per volt/cm in different flames.

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* For small values of X.

Since the mobility of the negative ions in flames is so much greater than that of the positive ions it appears probable that the negative ions are free electrons. This was first pointed out by Lenard about 1903.

The "mobility constant" K defined by the equation $K=(p/760)(273/T)k_2$ for the electrons in a flame at 2000°K is therefore about equal to (273/2000) 3000 or about 400. The motion of electrons in gases at the ordinary temperature is discussed by K. T. Compton and I. Langmuir.[8] According to K. T. Compton's theoretical formula we should expect K to vary inversely as $T^{1/2}$ so that if $K=400$ at 2000°K then it should be equal to about 1000 at 300°K. The mobility constant is very different in different gases so that it is difficult to say what it might be expected to be in such a mixture of gases as we have in a flame. The gases in a flame are mostly nitrogen, steam, carbon monoxide and carbon dioxide. In carbon dioxide Townsend found the velocity of electrons to be 1.2×10^5 cm/sec with $X/p=0.25$ at about 300°K. This gives K equal to about 600 which may be compared with the value 1000 in a flame.

There seems no reason therefore, to suppose that the mobility of the electrons in flames deduced from the Hall effect is not approximately correct. The mobility constant in pure nitrogen at 300°K is equal to about 8000 for small values of X/p which is eight times larger than the value deduced from the results in flames. It has therefore been suggested that the electrons in flames are only free part of the time so that the mobility observed is not that of free electrons but an average mobility of electrons and negative ions. It is however easy to show that the Hall effect must give the mobility of the free electrons even if the electrons are not free all the time.

Let the flame contain n_1 positive ions per cc, n_2 negative ions and n_3 electrons. We may suppose that the positive and negative ions have equal mobilities so that the upward velocities in the flame are given by

$$v_1 = V + \frac{k_1}{e}(Ye - Hek_1X)$$

$$v_2 = V + \frac{k_1}{e}(-Ye - Hek_1X)$$

$$v_3 = V + \frac{k_2}{e}(-Ye - Hek_2X).$$

The upward current is equal to $e(n_1v_1-n_2v_2-n_3v_3)$ and we have also $n_1=n_2+n_3$ so that since the upward current must be zero we get:

$$\frac{Y}{HX} = \frac{n_3(k_1^2 - k_2^2)}{k_1(n_1 + n_2) + n_3k_2}.$$

Since k_1/k_2 is very small this gives approximately

$$-\frac{Y}{k_2HX} = 1 - \frac{k_1(n_1 + n_2)}{k_1(n_1 + n_2) + n_3k_2}$$

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[8] K. T. Compton and I. Langmuir, Rev. Mod. Phys. **2**, 204 (1930).

If we put $\bar{k}=[k_1(n_1+n_2)+n_3k_2]/(n_1+n_2+n_3)$ so that $\bar{k}$ is the average mobility of all the ions and electrons then this becomes

$$-\frac{Y}{k_2HX}=1-\frac{k_1(n_1+n_2)}{\bar{k}(n_1+n_2+n_3)}.$$

Now k_1 is equal to about 2 and the average mobility cannot be less than say 1000 since the Hall effect gives about 3000 so that the last term in the above equation cannot be greater than about 1/500. Hence we must have very approximately $k_2=-Y/HX$. Thus even if the electrons are only free part of the time, the Hall effect, nevertheless, gives the mobility of the electrons while they are free.

The small value of the mobility of the electrons in flames is no doubt due to the presence of carbon dioxide and other similar gases since the mobility in carbon dioxide is known to be small at ordinary temperatures.

3. The Effect of a Magnetic Field on the Conductivity of a Bunsen Flame

The conductivity in the uniform region of a Bunsen flame is altered by a transverse magnetic field. This effect can be studied with an apparatus similar to that used for measuring the Hall effect. The two wires *EE* are turned so that they lie in a horizontal plane parallel to the direction of the current and the potential difference between them is measured with the quadrant electrometer. The current through the flame divided by this potential difference is proportional to the conductivity.

The resistance of the flame can be measured with a Wheatstone bridge. If the cathode is coated with lime and baryta the current is nearly proportional to the potential difference between the electrodes so that the resistance given by the bridge is nearly independent of the potential difference used. It increases slowly as the potential difference is increased. The resistance is of the order of one million ohms with a pure flame and much smaller with a flame containing alkali salt vapor.

If R denotes the resistance and δR the change due to a transverse magnetic field H then it is found that

$$\delta R/R = AH^2 + BH$$

approximately, where A and B are constants.

The writer[9] found $A=3.1\times10^{-9}$ and $B=1.5\times10^{-5}$ for a pure flame. In these experiments the current and potential gradient were measured. A new series of measurements has been made, during the preparation of this article, by H. G. Montgomery who measured the resistance with a Wheatstone bridge. He finds $A=4.85\times10^{-10}$ and $B=3.2\times10^{-6}$ for a pure flame.

Since the mobility of the electrons is much greater than that of the positive ions we should expect the effect of the magnetic field on the resistance to be similar to the effect of a magnetic field on the resistance of a metal on the classical electron theory of metallic conduction. In a flame the electron con-

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[9] H. A. Wilson, Proc. Roy. Soc. **A82**, (1909).

centration is so small that the Maxwell velocity distribution should hold for the electrons. For a metal on the classical theory Gans finds $\delta R/R=(9\pi/64)(4-\pi)k_2^2H^2$ or $\delta R/R=0.4\ k_2^2H^2$ approximately. Approximate theories in which the velocity distribution of the electrons is neglected make $\delta R/R$ very small. The effect of the magnetic field on the resistance is a second order effect and so cannot be calculated by approximate methods. The Hall effect is a first order effect and so can be calculated approximately by assuming all the electrons to have the same velocity of agitation. With $A=4.85\times10^{-10}$ this gives $0.4k_2^2=4.85\times10^{-10}$ so that $k_2=3.5\times10^{-5}$ or $k_2=3500$ cm/sec. per volt/cm. This is not far from C. H. Kean's mean value $k_2=3900$ for a pure flame.

The flames used by Montgomery and Kean were quite similar. Thus the term AH^2 in the equation $\delta R/R=AH^2+BH$ seems to have about the value which might be expected.

The term BH is evidently due to the induced e.m.f. in the flame due to its upward velocity V. If d is the distance between the electrodes the induced e.m.f. is equal to $VHd/10^8$ volts. If P is the potential fall in the uniform field between the electrodes then we should expect to have $\delta R/R=VHd/10^8\ P$ so that $B=Vd/10^8P$. The velocity V is about 300 cm/sec. and d was about 10 cm. With $V=300$, $d=10$, and $P=10$ this gives $B=300\times10/10\times10^8=3\times10^{-6}$ which is about what Montgomery found. In Montgomery's experiments the total P.D. between the electrodes was usually about 20 volts so that P may well have been about 10 volts. In the writer's experiments, however, P was supposed to be about 100 volts for 10 cm so that $B=Vd/P10^8=3000/10^{10}=3\times10^{-7}$ whereas the experiments gave $B=1.5\times10^{-5}$. The reason for this discrepancy is not known but since it does not appear in Montgomery's work it seems likely that the writer in some way greatly overestimated the value of P. With P equal to 2 volts instead of 100 we get $Vd/P10^8=3000/2\times10^8=1.5\times10^{-5}$.

It has been suggested[10] that the abnormally large value of the term BH found by the writer may have been due to an effect of the force on the current through the flame in the magnetic field.

If i is the current density, the force on unit volume of the flame is Hi so that $\rho(dV/dt)=Hi$ where V is the upward velocity and ρ the density of the flame gases. This gives $Hit=\rho(V_2-V_1)$ where t is the time in which the velocity changes from V_1 to V_2. If we take V_1 to be the velocity at the bottom and V_2 that at the top of the flame then $h=\frac{1}{2}(V_1+V_2)t$ where h is the height of the flame so that $V_2^2-V_1^2=2Hih/\rho$. If b is the thickness of the flame then the total current C is given by $C=ihb$ so that $V_2^2-V_1^2=2HC/\rho b$. For Montgomery's pure flame b was about one cm, ρ about 2×10^{-4} and C about 3×10^{-5} ampere. With $H=5000$ and $V_1=300$ this gives $V_2^2=9\times10^4+(10^4\times3\times10^{-6})/(2\times10^{-4}\times1)$ so that $V_2=300.3$. Thus in this case the force in question has no appreciable effect on the velocity of the flame. J. S. Watt with a highly conducting flame containing potassium through which he passed a current of 4×10^{-2} ampere found that the upward motion of the

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[10] C. W. Heaps, Phys. Rev. December (1924).

flame was stopped with the magnetic field in one direction and greatly accelerated with it in the other direction. With $C=4\times10^{-2}$ ampere and $H=5000$ we get $V_2^2=9\times10^4+(10^4\times4\times10^{-3})/(2\times10^{-4})$ which gives $V_2=538$ cm/sec. Thus, in this case the force on the flame increases the velocity from 300 to 538 and with the field reversed the velocity would be reduced to zero before the top of the flame was reached. The force on the flame is therefore quite adequate to explain Watt's result. In the writer's and in Montgomery's and Kean's experiments the magnetic field never had any observable effect on the appearance of the flame.

The value of the horizontal electric field X in Montgomery's experiments was not more than about 4 volts per cm. C. W. Heaps[11] made a series of measurements on the effect of a magnetic field on the conductivity of a flame in which he used fields up to 168 volts/cm. In these experiments the current was passed through the flame in a vertical direction between electrodes consisting of horizontal wire gratings. The potential gradient in the flame was measured by means of two probe wires connected to an insulated electrometer. It was found that there was a point between the electrodes at which the magnetic field did not change the potential gradient so that at this point the change in the current could be used as a measure of the change in the conductivity due to the magnetic field. The potential gradient was not uniform. Heaps found the following values of $\delta C/C$, C being the current. The magnetic field was 3600 gauss in each case.

X(volts/cm)	19	31	69	125	168
$-\delta C/C$	0.09	0.29	0.54	0.52	0.50

If we put $-\delta C/C$ equal to $\delta R/R$ and $\delta R/R=0.4k_2^2H^2$ we get $0.5=0.4k_2^2(3600)^2$ which gives $k_2=31{,}000$ cm/sec. per volt/cm. This is about ten times the value given by the Hall effect and by Montgomery's value of $\delta R/R$ for small values of X. I think it is probable that owing to X not being uniform in Heap's experiments the theory which gives $\delta R/R=0.4k_2^2H^2$ is not applicable to them.

If k_2 were equal to about 3000 for small values of X and to 30,000 for large values this would indicate that the negative ions are free electrons when X is large but that when X is small they are not all free electrons at any instant so that k_2 is then an average value for electrons and ions. As explained above this idea does not appear to be admissible in the case of the values of k_2 given by the Hall effect. The fact that the current through the flame seems to be proportional to the potential gradient seems to show that k_2 does not increase with X but it would be worth while to investigate this point further.

4. The Conductivity of Flames Containing Alkali Metal Salts

The conductivity of a flame containing alkali salt vapors was studied by Arrhenius[12] in 1891 and by Smithells, Dawson and the writer[13] in 1899. Since

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[11] C. W. Heaps, Phys. Rev. **7**, June (1916).

[12] Arrhenius, Ann. d. Phys. u. Chem. **42**, 30, 33 (1891).

[13] Smithells, Dawson & Wilson, Phil. Trans. **A193**, 98 (1900).

then many results on the conductivity have been published by different physicists with not very concordant results. In the earlier experiments the current between two platinum electrodes a few millimeters apart in the flame was used as a measure of the conductivity. When the potential difference used is not more than a fraction of a volt the current is nearly proportional to the P.D. so that the conductivity is proportional to the current. The electrodes are much cooler than the flame gases so that the temperature of the gases between them must be somewhat lower than that of the rest of the flame. The flame is at about 2000°K and platinum electrodes in it usually have a temperature not above 1600°K.

In the more recent experiments the ratio of the current to the uniform potential gradient between the electrodes has been used as a measure of the conductivity. This ratio is independent of the potential gradient and is proportional to the conductivity of the flame. In this way the conductivity at a distance from the electrodes is obtained.

The apparatus shown in Figure 5 is suitable for studying the variation of the conductivity with the concentration of the salt in the flame and the relative conductivities due to salts of different metals. Two similar quartz tube burners provided with sprayers S and S' are used both like the burner described in Section 1. A current from a battery P is passed through the two flames in series between the platinum electrodes AB and $A'B'$. The potential gradients in the two flames can be compared by means of two pairs of insulated platinum probe wires E_1E_2 and $E_1'E_2'$ either of which can be connected to an insulated quadrant electrometer Q by means of a commutator K.

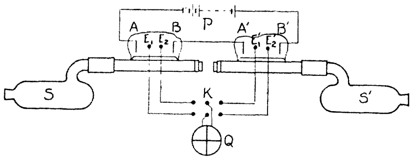

Fig. 5. Apparatus for studying variation of conductivity with concentration of the salt in flame and relative conductivities due to salts of different metals.

The two sprayers are supplied with gas and air from the same sources so that any fluctuations affect both flames equally. The burners and sprayers are adjusted so that the two flames have nearly equal conductivities when the same solution is used in both sprayers.

To find the relative conductivities, c_1 and c_2 of the flame F when two solutions, say S_1 and S_2 are sprayed into it a solution is sprayed into the other flame F' giving a conductivity about half way between c_1 and c_2. The solution S_1 is then sprayed into F and the electrometer deflections d_1 and d_1' due to the two flames observed. The solution S_2 is then sprayed into F and the electrometer deflections d_2 and d_2' again observed. The ratio of the conductivities of the flame F is then given by $c_1/c_2 = d_2d_1'/d_1d_2'$ because the deflections are inversely as the conductivities. The second flame F' merely serves for comparison with the first flame so eliminating as far as possible errors due to variations in the gas and air supplies. The gas and air pressures should be measured and kept as nearly constant as possible by means of regulators.

Relative conductivities have been studied with apparatus like that just described by the writer,[14] A. B. Bryan[15] and during the preparation of this article by R. F. Weichert.

The conductivity in reciprocal ohms per cc of a flame and the concentration of the metal in it have been measured by B. T. Barnes,[16] E. Zachmann[17] and J. A. J. Bennett.[18]

Barnes and Bennett used a flame and electrodes like those used by H. E. Banta described in Section 1. The anode consisted of a small platinum disk with its plane vertical surrounded by a guard ring. In this way the current density near the anode was found and the potential gradient near it was measured by means of two probe wires connected to an electrometer. The amount of solution entering the flame per second was determined by finding the decrease in the amount of salt in the sprayer after running it for a known time and the volume of the flame gases was found by measuring the upward velocity of the flame and its horizontal cross section. Bennett found that the mols of metal per cc in the flame at 1920°K was equal to the concentration of the solution sprayed in mols per liter (g) multiplied by 1.71×10^{-10}.

E. Zachmann used a flame having a circular horizontal cross section and passed the current through it in a vertical direction. The burner was used as the lower electrode and the upper electrode consisted of a heavy metal grating which was kept cold. The potential gradient between the electrodes was measured by means of two probe wires connected to an electrometer. The conductivity of the flame was calculated on the assumption that the current was uniformly distributed over the horizontal section of the flame. There was a very great resistance in the layers of cool gas at the cold electrodes so that it was necessary to use large potential differences to get enough current through the flame to make the potential gradient large enough to be measured. The potential gradients were very small, usually not more than 0.1 volt per cm and the distance over which the gradient was nearly uniform was about 10 to 15 mm. The P.D. between the two probe wires was therefore not more than about 0.1 volt. The potential of a probe wire in a flame usually fluctuates to some extent, due to temperature variations and other causes, so that it is difficult to measure very small potential differences accurately. This is a serious objection to the use of cold electrodes and there does not appear to be any good reason why hot electrodes with the cathode coated with CaO and BaO should not be used. The emission of electrons by an oxide coated cathode should not affect the conductivity in the uniform gradient at some distance from the cathode. However, Zachmann succeeded in making measurements of the conductivity in spite of the very small potential gradients

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[14] H. A. Wilson, Phil. Trans. **A216,** 63 (1915).

[15] A. B. Bryan, Phys. Rev. October, 1921.

[16] B. T. Barnes, Phys. Rev. (2) **23,** 178 (1924).

[17] E. Zachmann, Ann. d. Physik **74,** 467 (1924).

[18] J. A. J. Bennett, Phil. Mag. (7) **3,** 127 (1927).

which he obtained and there does not appear to be any reason why his method should not give approximately correct results. Zachmann determined the concentration of the metal in the flame by methods similar to those used by Barnes and by Bennett.

The most serious source of error in these measurements of relative conductivities is the variability of the sprayers. A very small change in a sprayer may produce a large change in the amount of salt which it delivers to the flame. It is therefore important if possible, to compare the conductivities due to the different metals by a method which is independent of the efficiency of the sprayer. Arrhenius found that the conductivity due to any alkali metal is roughly proportional to the square root of the concentration of the metal in the flame.

The experimental results obtained by different observers for potassium salts are shown graphically in Figure 6. The vertical coordinate (y) is equal to $g/(c^2-1)$ where g denotes the mols of metal per liter in the solution sprayed and c the conductivity taking $c=1$ for the pure flame. The horizontal coordinate (x) is equal to $1000c^{-1}$.

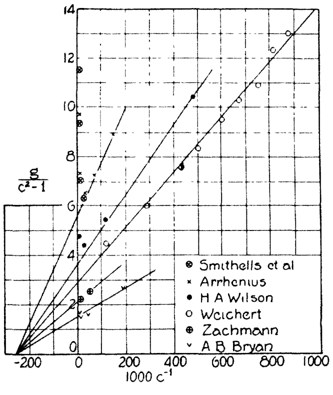

Fig. 6. Relative conductivities obtained by different observers for potassium salts.

It appears that the points for values of 1000 c^{-1} greater than about 50 lie on straight lines which all pass through the point A at $y=0$, $x=-260$. Thus when the conductivity is less than 20 we have $g/(c^2-1)=a+bc^{-1}$ and the ratio a/b is equal to about 0.26 for the results obtained by all the different observers. When c is greater than 20, then $g/(c^2-1)$ increases as c increases. The results of Smithell's *et al* are all for large values of c and so do not show the linear relation between $g/(c^2-1)$ and 1000 c^{-1}. Weichert's results are all for small values of c and so do not show the increase as c^{-1} decreases. The difference between the slopes of the straight lines is due, of course, to the differences between the sprayers and burners used by the different observers.

The ratio a/b is independent of the sprayer efficiency and so affords a satisfactory measure of the conductivity. Weichert's experiments were done, under my direction, during the preparation of this article. It was thought that some of the previous work might have been affected by errors due to impurities in the salts and water used in making up the solutions. In Weichert's experiments the water used was re-distilled in a fused quartz still and was kept in fused quartz flasks. It was found that this water did not increase the conductivity of the flame while ordinary distilled water usually increased it considerably. The solutions were made up in quartz flasks and the sprayers used were made of fused quartz. The burners were quartz tubes with slots cut in them as described above.

Figure 7 shows the same results as Figure 6 but the values of $g/(c^2-1)$ have been multiplied by the following factors: Arrhenius 0.0514, Smithells *et al* 0.5, A. B. Bryan 1.000, H. A. Wilson 0.788, Weichert 1, Zachmann 0.1400. It will be seen that nearly all the points fall very near to the straight line drawn. Thus it appears that the results of the different observers using very different methods are in very good agreement as regards the relation between the relative conductivity and the concentration of the metal in the flame. Probably a small change in the temperature of the flame alters the conductivity of the pure flame in about the same ratio as that of the salted flame and so does not change the relative conductivity.

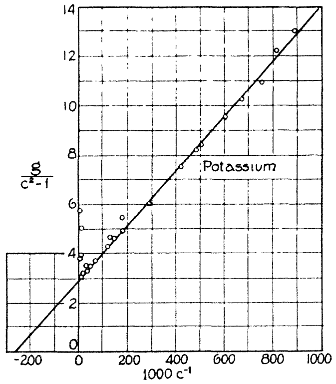

Fig. 7. Same results as Fig. 6 except ordinates are multiplied by following factors: Arrhenius 0.0514, Smithells et al 0.5, A. B. Bryan 1.000, H. A. Wilson 0.788, Weichert 1, Zachmann 0.1400.

It appears that $g/(c^2-1)$ has a minimum near to $c=30$. For values of c rather near this value say from $c=15$ to $c=100$ the value of $g/(c^2-1)$ is nearly constant so that the conductivity is proportional to the square root of the concentration. But for $c>100$ or $c<15$ the conductivity does not vary as the square root of the concentration. Thus for example, Zachmann's measurements with potassium are for conductivities of 15 and 50 and he concluded that the conductivity varies as the square root of the concentration. When c changes from 15 to 100 the concentration changes by a factor of about 45 so that there is a considerable range of concentration in which c varies very nearly as $g^{1/2}$.

The theory of the variation of the conductivity with the concentration of the metal vapor in the flame will now be considered. We may suppose that the conductivity is due to the presence of electrons formed by dissociation of the metal atoms and flame gases. If M denotes a metal atom, M_+ a positive metal ion and e an electron then $M = M_+ + e$ and for a flame gas atom $F = F_+ + e$. If p_1 is the partial pressure of the neutral metal atoms, p_2 that of the metal positive ions and p_3 that of the electrons then $K = p_2 p_3 / p_1$ is the equilibrium constant for the metal vapor. In the same way $K' = p_2' p_3 / p_1'$ where p_1' and p_2' are the partial pressures of the neutral flame atoms and flame positive ions.

The conductivity S is proportional to the number of electrons per cm^3 so we may put $p_3 = AS$ where A is a constant. Also the number of metal atoms per cm^3 in the flame is proportional to the concentration of the solution sprayed so that $p_1 + p_2 = Bg$ where g is the concentration of the solution in gram atoms of metal per liter and B a constant. We have also in the uniform potential gradient between the electrodes $p_2 + p_2' = p_3$.

Since $p_2 = Kp_1/p_3$, $p_2' = K'p_1'/p_3$ and $AS = p_3 = p_2 + p_1$ we get

$$AS = Kp_1/AS + K'p_1'/AS.$$

Also $p_1 + p_2 = Bg$ with $p_2 = Kp_1/p_3$ gives $p_1 = ASBg/(K + AS)$ and in the same way putting $p_1' + p_2' = p_F$ we get $p_1' = ASp_F/(K' + AS)$ so that

$$AS = \frac{KBg}{K + AS} + \frac{K'p_F}{K' + AS}\cdot$$

Now $K' = p_2' p_3 / p_1'$ and p_1' is of the order of one atmosphere while p_2' and p_3 are of the order of 10^{-10} atmosphere so that K' is of the order of 10^{-20}. $Ac = p_3$ so that K' is always quite negligible compared with AS and therefore

$$S = \frac{KBg}{A(K + AS)} + \frac{K'p_F}{A^2 S}\cdot$$

Let S_0 denote the conductivity of the pure flame so that $S_0 = K'p_F / A^2 S_0$ and so

$$S = \frac{KBg}{A(K + AS)} + \frac{S_0^2}{S}$$

or

$$\frac{S^2 - S_0^2}{S^2} = \frac{KBg}{A(K + AS)}$$

so that

$$\frac{g}{S^2 - S_0^2} = \frac{A^2}{KB} + \frac{A}{B} S^{-1}.$$

Now let $c = S/S_0$ so that

$$\frac{g}{c^2 - 1} = \frac{A^2 S_0^2}{KB} + \frac{AS_0}{B} c^{-1}.$$

Let $a = A^2S_0^2/KB$ and $b = AS_0/B$ so that

$$\frac{g}{c^2 - 1} = a + bc^{-1}$$

so that $K = AS_0b/a$. Also $b^2/a = K/B$ so that $K = Bb^2/a$. It appears that we should expect to have a linear relation between $g/(c^2-1)$ and c^{-1} and also that the ratio b/a should be independent of the constant B which is determined by the working of the sprayer and burner. The results obtained with potassium with small values of the conductivity agree very well with these deductions from the theory.

The increase in $g/(c^2-1)$ with c when c is large is probably due to condensation of metal vapor on the electrons converting them into negative ions of low mobility and so diminishing the conductivity. Another possible explanation is that when the concentration of the solution sprayed is large the salt is not completely converted into metal vapor in the flame. The second explanation, however, appears to be incompatible with the fact that the light emitted by a sodium flame per cm^2 is a function of the mass of sodium per cm^2 and independent of the concentration of the sodium. That is the light from unit area of a flame of thickness d containing S grams of sodium per cc is a function of the product Sd. The light is certainly emitted by neutral sodium atoms so that it follows that the mass of neutral sodium atoms in the flame is proportional to the amount of sodium present per cm^2. The fraction of the sodium converted into metal vapor is therefore independent of the concentration of the sodium in the flame. The same thing is true for the other alkali metals. If the fraction converted into metal vapor is independent of the concentration it seems probable that this fraction is equal to unity.

The relative conductivities due to the dissociation of metal atoms into electrons and positive ions without formation of negative ions of low mobility must therefore be obtained from the results with small concentrations.

Since $K = AS_0b/a$ the equilibrium constant is proportional to b/a. The straight line asymptote in Figure 7 cuts the X-axis at $1000\,c^{-1} = -260$. This length is equal to $1000\,a/b$ so that b/a for potassium is equal to 3.85. This number is based on the results of Arrhenius, H. A. Wilson, A. B. Bryan, Zachmann and Weichert. It is presumably more reliable than a value derived from any single set of observations.

The value of the equilibrium constant K may be obtained by multiplying b/a by AS_0 and AS_0 is equal to the partial pressure p_{30} of the electrons in the pure flame. A rough value of this pressure may be calculated from the absolute value of the conductivity and the mobility of the electrons. J. A. J. Bennett found the conductivity of his flame to be 3.17×10^{-7} ohms at 1920°K and we may take k_2 for the electrons to be 3900 cm/sec per volt/cm which is the value obtained by C. H. Kean from the Hall effect. We have then $p_{30} = nkT$ where n is the number of electrons per cm^3 and k the gas constant for one molecule. Also $S_0 = nek_2$ so that

$$p_{30} = \frac{S_0kT}{ek_2} = \frac{S_0NkT}{Nek_2}$$

where N is the number of molecules in one mol. But $Nk=82$ for p in atmospheres and $Ne=96{,}500$ coulombs so that

$$p_{30}=\frac{3.17\times 10^{-7}\times 82}{3900\times 96500}=1.325\times 10^{-10}\text{ atm}.$$

Hence we get $K=p_{30}b/a=3.85\times 1.325\times 10^{-10}=5.1\times 10^{-10}$ for potassium.

The value of b/a may easily be wrong by 10 percent or more. The conductivity of the pure flame may also differ considerably from 3.17×10^{-7}. Thus the writer got 5×10^{-7} and Zachmann got 6×10^{-7}. It is therefore only possible to get the order of magnitude of the equilibrium constant in this way.

Barnes and Bennett both estimated the equilibrium constant in another way by using the equation $K=B(b^2/a)$. They determined B by finding the concentration of the metal in the flame when spraying a solution of known concentration. The constant B can be found in this way fairly accurately but the possible error in b^2/a is greater than that in b/a. Let the mols of metal per cc in the flame be equal to Gg. We have then $p_1+p_2=GgR\theta=Bg$ so that $B=GR\theta$ and $K=GR\theta b^2/a$. Barnes found G to be about 2×10^{-10} and Bennett got $G=1.7\times 10^{-10}$. In the case of potassium we have $b/a=3.85$ and we get $b=1.1\times 10^{-5}$ from Figure 7 so that we have $K=1.7\times 10^{-10}\times 82\times 1920\times 3.85\times 1.1\times 10^{-5}=11.3\times 10^{-10}$. This is about double the previous value which is probably the more reliable of the two.

The mobility of the negative ions can be calculated when G and the conductivity of the pure flame S_0 in reciprocal ohms per cm³ are known. Thus, using Bennett's values $G=1.7\times 10^{-10}$ and $S_0=3.17\times 10^{-7}$ we get

$$K=GR\theta\frac{b^2}{a}=\frac{b}{a}\,\frac{S_0R\theta}{Nek_2}$$

so that

$$k_2=\frac{S_0}{NebG}=\frac{3.17\times 10^{-7}}{96500\times 8.4\times 10^{-6}\times 1.7\times 10^{-10}}$$

which gives $k_2=2530$ cm/sec per volt/cm. This result is as near as could be expected to the value of k_2 deduced from the Hall effect.

Theoretical values of K may be calculated by means of the thermodynamical theory of the reaction $M=M_{+}+e$ worked out by Saha. According to this theory

$$\log_{10}K=-\frac{5048V}{\theta}+2.5\log\theta-6.56$$

where V is the ionization potential of the metal in volts and θ the absolute temperature. V for potassium is 4.317 volts so that this equation gives $K=6.2\times 10^{-10}$ for potassium at 2000°K. The values $K=5.1\times 10^{-10}$ and 11.3×10^{-10} deduced from the experimental results on flames agree with this as well as could be expected. This was first shown to be the case by A. A. Noyes and the writer in 1923.

The results reported with caesium, rubidium, sodium and lithium by the different observers do not agree as well as in the case of potassium. When $g/(c^2-1)$ and 1000 c^{-1} are plotted it is not always possible to make all the points lie on a single curve by multiplying the g's by a suitable sprayer factor. This may probably be attributed to errors due to irregular action of the sprayers used.

In the case of caesium the results for very small concentrations obtained by the writer, A. B. Bryan, B. T. Barnes, and J. A. J. Bennett agree in giving a linear relation between $g/(c^2-1)$ and 1000 c^{-1}. The results for larger concentrations indicate that $g/(c^2-1)$ increases as c increases, as with potassium, but do not agree well and so may be ignored. Results for larger concentrations are given by Arrhenius, Smithell *et al* and the writer.

In the case of rubidium all the points can be made to lie near a single curve but do not fall exactly on it.

The results for small concentrations of caesium and rubidium are shown in Figure 8. The values of $g/(c^2-1)$ have been multiplied by sprayer factors as was done with potassium. The straight line asymptotes meet the x-axis at -30 for caesium and -110 for rubidium. This makes b/a equal to 33 for caesium and 9 for rubidium. The equilibrium constant K is therefore equal to 44×10^{-10} for caesium and 12×10^{-10} for rubidium. These values, especially that for rubidium, are subject to large possible errors.

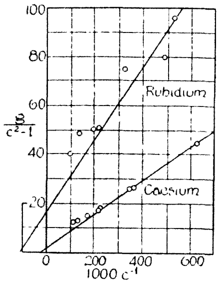

Fig. 8. Conductivities for small concentrations of caesium and rubidium. The values of $g/(c^2-1)$ have been multiplied by sprayer factors as was done with potassium.

In the case of sodium the results of Weichert, Bryan and Smithells *et al* agree well but those of Arrhenius, Zachmann and the writer cannot be made to agree by the use of any sprayer factors. Weichert's experiments were done with a specially purified sample of sodium chloride very kindly prepared by Dr. Scott of the chemical department of the Rice Institute. Weichert's solutions were made up in quartz vessels and he used quartz sprayers as already mentioned.

In the case of lithium the results of Weichert and Smithells *et al* can be made to agree but not those of Arrhenius and Zachmann.

Figure 9 shows the results of Weichert, Bryan and Smithells for sodium and Figure 10 those of Weichert and Smithells for lithium.

With sodium and lithium the conductivity is smaller than with caesium, rubidium and potassium and $g/(c^2-1)$ decreases as $1000\ c^{-1}$ increases up to larger values of $1000\ c^{-1}$. The linear increase with the smaller concentrations is shown by the results for sodium but not with lithium. The observations with small concentrations are not sufficiently numerous in either case to fix the position of the asymptote with any certainty.

In the equation $y=bc^{-1}+a$ of the asymptote the constant $b=AS_0/B$ should, according to the theory, have the same value for all the metals. This is approximately true for caesium, rubidium, and potassium. We may therefore assume that b has the same value for sodium and lithium as for caesium, rubidium and potassium. Making this assumption enables the asymptotes to be drawn as shown in Figures 9 and 10. These asymptotes cut the x-axis at -3000 for sodium and about -6000 for lithium. Hence $b/a=0.33$ for sodium and 0.16 for lithium. The equilibrium constant K is therefore equal to 0.45×10^{-10} for sodium and to 0.23×10^{-10} for lithium.

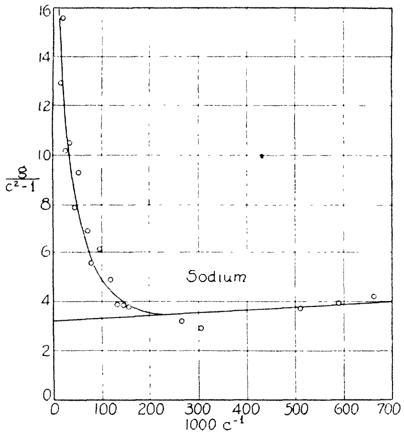

Fig. 9. Results of Weichert, Bryan and Smithells for sodium.

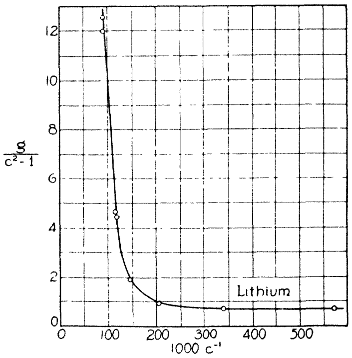

Fig. 10. Results of Weichert and Smithells for lithium.

Table V gives the values of K found from the flame conductivities and those calculated by means of Saha's theory all multiplied by 10^{10}. It appears that the values of K found for caesium rubidium, and potassium agree about as well as could be expected with those calculated but that the values found for sodium and lithium are much larger than the theoretical values.

TABLE V. *Values of K found from flame conductivities and calculated from Saha's theory.*

Metal	b/a	K (found)	K (calculated) 2000° K	1950° K
Caesium	33	44	83.0	44.16
Rubidium	9	12	16.33	8.22
Potassium	3.85	5.1	6.21	3.06
Sodium	0.33	0.45	0.0621	0.0272
Lithium	0.16	0.23	0.0142	0.0060

The conductivity due to equal concentrations is nearly proportional to $K^{1/2}$ so it appears that whereas according to Saha's theory potassium should give ten times as much conductivity as sodium the experiments only indicate about 3.4 times as much. There seems therefore, to be a definite failure of Saha's theory in the case of sodium and lithium. A. A. Noyes and the writer using the results obtained by the writer in 1915 concluded that sodium and lithium give conductivities roughly in agreement with Saha's theory. This conclusion was based on the relative conductivities for large concentrations which were supposed to be proportional to the square root of the concentration. But it now appears that the conductivity for large concentrations is not proportional to the square root of the concentration. The equilibrium constants calculated by Noyes and the writer for sodium and lithium were therefore considerably too small.

If we compare the concentrations required to give $c=40$ for potassium and sodium we get $g/(c^2-1)=0.34\times10^{-5}$ for potassium and $g/(c^2-1)=10.5\times10^{-5}$ for sodium. This makes g for sodium 36 times g for potassium so that if the conductivity varied as the square root of the concentration the conductivity due to equal concentrations would be 6 times as great for potassium as for sodium. But near $c=40$ the value of $g/(c^2-1)$ for sodium decreases rapidly as $1000\ c^{-1}$ increases.

Table VI gives the values of the ionization potential (V) calculated from the values of K deduced from the flame conductivities and the values deduced from the limits of the principal spectral series:

TABLE VI. *Ionization potentials calculated from the values of K and from spectroscopic data.*

Metal	V (from flame experiments)	V (from limits of series)
Caesium	3.97	3.87
Rubidium	4.20	4.15
Potassium	4.35	4.32
Sodium	4.77	5.12
Lithium	4.88	5.36

It may well be asked how it is that Arrhenius, Smithells, *et al*, the writer, Zachmann, Moreau and others all concluded that the conductivity due to alkali metals varies nearly as the square root of the concentration if this is not actually the case. The reason is that there is a very considerable range of concentration for each metal in which the conductivity is nearly as the square root of the concentration. Thus in the case of sodium Weichert's results show that $g/(c^2-1)$ is equal to about 3.5×10^{-5} for values of $1000\ c^{-1}$ between 130 and 700. This shows that c^2-1 is nearly proportional to g for values of g between 210×10^{-5} and 3.7×10^{-5}. Many of the measurements made happened to fall in the range in which c was nearly proportional to $g^{1/2}$.

TABLE VII. *Relative conductives found by Weichert.*

KCl		NaCl		LiCl	
10^5g	c	10^5g	c	10^5g	c
26.73	7.65	684.2	10.58	13684	10.72
6.682	3.50	342	8.48	3421	8.65
3.341	2.33	171	6.79	855	6.80
2.506	2.00	42.8	3.79	214	4.85
1.670	1.66	10.69	1.96	53.5	2.92
1.253	1.49	5.345	1.51	13.4	1.75
0.835	1.33				
0.627	1.23				
0.418	1.15				

5. THE VARIATION OF THE CONDUCTIVITY WITH THE TEMPERATURE AND PRESSURE

J. A. J. Bennett[19] is the only observer who has investigated the variation of the conductivity with the temperature. He varied the temperature by altering the gas supply and by adding carbon dioxide to the flame. In this way he was able to change the temperature from 1570°K to 1920°K. The temperature was measured by an optical method. A strong solution of a sodium salt was sprayed into the flame and a beam of white light from an incandescent lamp was passed through the flame. The spectrum of the light was observed and the temperature of the filament was adjusted until the sodium *D* lines were not visible in it so that the absorption by the sodium vapor was equal to the emission. The temperature of the filament is then the same[20] as that of the flame and was found with an optical pyrometer.

Tables VIII and IX give Bennett's results for caesium and rubidium

TABLE VIII. *Conductivities of flames of various temperatures containing CsCl in varying concentration of solution (Bennett).*

Temperature	Conductivities, S, for various concentrations, g				
	$g=0.31\times10^{-4}$	$g=0.62\times10^{-4}$	$g=1.25\times10^{-4}$	$g=2.5\times10^{-4}$	$g=5\times10^{-4}$
1920 °K	$S=1.45\times10^{-6}$	2.37×10^{-6}	3.81×10^{-6}	7.13×10^{-6}	12.1×10^{-6}
1870	1.35	1.83	3.13	5.61	9.3
1720	0.69	1.11	1.69	2.91	4.22
1670	0.58	0.87	1.32	2.39	3.40
1570	0.46	0.76	1.03	1.75	2.55

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[19] J. A. J. Bennett, Phil. Mag. January (1927).

[20] H. Kohn, Ann. d. Physik **44**, No. 5. June (1914).

chlorides. g is the concentration of the solution sprayed in mols per liter and S the conductivity of the flame in ohms^{-1}/cm^3.

TABLE IX. *Conductivities of flames of various temperatures containing RbCl in varying concentrations of solution (Bennett).*

Temperature	Conductivities, S, for various concentrations, g $g=2\times10^{-5}$	$g=5\times10^{-5}$	$g=10\times10^{-5}$
1920° K	$S=6.5\times10^{-7}$	9.83×10^{-7}	16.35×10^{-7}
1870	5.28	8.10	12.60
1720	2.58	3.18	4.67
1670	2.00	2.45	3.40
1570	1.25	1.45	2.00

The sprayer factor G was found at each temperature and had the following values:

$10^{10}G$	1.71	1.62	2.21	2.36	2.37
degrees K	1920	1870	1720	1670	1570

The concentration in the flame in mols per cc is equal to gG. By plotting the values of the conductivity S against gG at each temperature we can find the values of the conductivity for constant concentrations in the flame. Table X gives some values found in this way for CsCl.

TABLE X. *Conductivities of flames of various temperatures for two values of the concentration of CsCl in the flame.*

Temperature	$gG=3\times10^{-14}$	$gG=9\times10^{-14}$
1570° K	$S=1.1\times10^{-6}$	$S=2.3\times10^{-6}$
1670	1.5	3.0
1720	1.85	3.8
1870	4.4	9.9
1920	5.3	12.6

The conductivity S is roughly proportional to $K^{1/2}$ so that since $\log_{10} K = -5048\,V/\theta + 2.5\log_{10}\theta + 6.56$ according to Saha's theory, we get

$$\log_{10}\frac{K_2}{K_1} = 2\log\frac{S_2}{S_1} = -5048V\left(\frac{1}{\theta_2}-\frac{1}{\theta_1}\right) + 2.5\log\frac{\theta_2}{\theta_1}$$

where S_1 and S_2 are the conductivities at θ_1 and θ_2. With $S_1=2.3\times10^{-6}$, $S_2=12.6\times10^{-6}$ and $\theta_1=1570$, $\theta_2=1920$ this gives $V=2.15$ volts which is about one half the value of V for caesium. The conductivity therefore does not appear to vary with the temperature as rapidly as might be expected according to Saha's theory.

The variation of the conductivity of a flame containing strontium with the pressure was investigated by da Andrade.[21] The current between two platinum electrodes in the flame was measured and a bead of strontium salt was put in the flame between the electrodes so that the salt vapor did not touch the electrodes. The current was found to be nearly inversely proportional to the square of the pressure from one to five atmospheres. In this experiment the temperature and the concentration of the salt vapor probably

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[21] da Andrade Phil. Mag. (6) **24,** 15 (1912).

varied with the pressure so that it is difficult to draw any very definite conclusions from the results.

6. The Conductivity of Flames for Rapidly Alternating Currents

The conductivity of a Bunsen flame for high frequency alternating currents has been investigated by the writer, E. Gold[22] and A. B. Bryan.[23] The current was passed through the flame between two concentric cylindrical electrodes of platinum. It was found that the apparent capacity of the electrodes was increased by the presence of the flame. Table XI contains A. B. Bryan's results. The first column gives the concentration of the solution of potassium carbonate which was sprayed into the flame. The P.D. given is the root mean square value between the electrodes. The capacity of the electrodes used was 8.23 $\mu\mu f$. It appears that the capacity varies nearly inversely as the cube root of the P.D. and about as the square root of the concentration of the solution sprayed. An approximate theory of the conductivity was given by the writer and E. Gold which was extended later by the writer and A. B. Bryan. This theory appears to agree roughly with the chief facts but is of too approximate a character to allow reliable values of the mobility and number of the electrons to be calculated.

TABLE XI. *Conductivity of flames for high frequency alternating currents (Bryan).*

Concentration (g/liter)	Frequency (cycles per sec.)	P. D. (volts)	Apparent capacity ($\mu\mu f$)	Apparent series resistance (ohms)
1.0	6×10^5	82.2	12.8	4500
1.0	6	66.7	13.75	4580
1.0	6	47.5	15.4	4550
1.0	6	26.9	18.4	6060
1.0	6	11.4	25.3	5000
1.0	10	21.15	20.6	2860
1.0	8	21.15	21.4	3470
1.0	6	21.15	23.5	4030
1.0	4	21.15	29.4	4700
1.0	2	21.15	39.8	4150
0.0	6	11.1	9.7	6420
0.1	6	11.1	15.7	7130
1.0	6	11.1	25.3	5170
5.0	6	11.1	39.3	3930
10.0	6	11.1	75.2	4560

7. The Vertical Potential Gradient in Flames

The temperature in an ordinary Bunsen flame is about 2000°K just above the inner cone and about 1900°K near the top of the flame. The ionization of an alkali metal in the flame therefore diminishes with the height above the inner cone. The electrons tend to diffuse upwards at a greater rate than the positive ions but since there cannot be any vertical current a vertical poten-

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[22] H. A. Wilson, E. Gold, Phil. Mag. April (1906).

[23] A. B. Bryan, H. A. Wilson, Phys. Rev. Feb. (1924).

tial gradient is set up which makes the upward velocity of the electrons equal to that of the positive ions.

If p denotes the partial pressure of the electrons, P the electrical potential and x the vertical height then we have

$$-\frac{dp}{dx} - ne\frac{dP}{dx} = 0$$

where e is the electronic charge and n the number of electrons per cc. But $p = nk\theta$ where k is the gas constant for one molecule and θ the absolute temperature. Hence

$$\frac{1}{p}\frac{dp}{dx} = -\frac{e}{k\theta}\frac{dP}{dx}.$$

According to Saha's theory:

$$\log\frac{p^2}{p_1} = \frac{Ve}{k\theta} + 2.5\log\theta + C$$

where V is the ionization potential and p_1 is the partial pressure of the neutral alkali metal atoms. We may suppose that p_1 is big enough for the ionization of the pure flame to be negligible. These two equations give

$$V = \frac{2(P' - P) + 5k(\theta' - \theta)/2e}{\log(\theta'/\theta)}.$$

Thus it should be possible to find the ionization potential V by measuring the potential difference $P' - P$ and the temperatures θ and θ' at two points in the flame. During the preparation of this article a series of experiments has been carried out by Mr. W. J. Taylor with the object of finding V in this way.

A Mecker burner was used which gave a flame about 3 cm in diameter. A horizontal grating of platinum wire was supported in the flame just above the inner cones. The P.D. between the grating and an insulated probe wire placed a few cm above the grating was measured with a quadrant electrometer. The probe wire was supported by a narrow quartz tube which covered it except for about 3 mm at its end. The temperatures of the flame at two levels above the grating were measured by the optical method described in Section 5 above. The potential difference between the two levels was found to be about 0.03 volt for a flame containing sodium when the temperature difference was about 30°. It was not possible to make accurate measurements of such small differences because of the unavoidable unsteadiness of the flame.

Taking the temperature of the flame at the lower level to be 1900°K we get

$$V = \frac{2 \times 0.03 - 10^{-4} \times 30}{30/187} = 3.7 \text{ volts}.$$

The results obtained for a sodium flame were usually between 3 and 4 volts which is probably as near to the ionization potential of sodium which is 5 volts as could be expected.

Similar experiments with a pure flame gave about 20 volts for the ionization potential. In this case the P.D. was about 0.4 volt. The ionization potentials of CO and H_2O are both about 13 volts while that of N_2 is about 18 volts. These experiments show that there is a vertical potential gradient in a Bunsen flame of about the magnitude to be expected on theoretical grounds.

8. Amplification of Electric Currents in a Flame

C. W. Heaps[24] found that by using a third electrode or grid between the anode and cathode in a Bunsen flame it is possible to obtain a large amplification of the current. The cathode was a platinum wire with its end bent upwards and coated at the tip with lime and baryta. The grid was a spiral wire of three turns about 0.65 cm in diameter which surrounded the tip of the cathode. The anode was a clean wire placed one cm below the cathode. The anode and cathode were connected to a battery giving 150 volts with a resistance R in the circuit. The grid was connected to the cathode through a grid battery. If I denotes the anode current and i the grid current then dI/di is the current amplification. dI/di was found to depend on R. It was 370 with $R=240$ ohms and 101.5 with $R=2\times10^6$. This arrangement can be used as a detector for electric waves.

9. Direct Determinations of the Mobility of the Electrons in Flames

The writer[25] in 1899 estimated the mobility of the negative ions in a flame by finding the potential gradient necessary to make them move down the flame. A great many experiments on the mobility of the negative ions have since been made by more or less similar methods. Accounts of such experiments have been published by Moreau, E. Gold, Wilckens, Lenard, E. Marx, and Kappler and others. The results obtained vary from 1000 to 20,000 cm/sec for one volt per cm. The great differences between the results obtained by different observers seem to show that such methods are not capable of giving reliable results. An account of these experiments is given in A. Becker's book.

10. Diffusion of Alkali Metal Vapors in Flames

When a small bead of an alkali metal salt, such as sodium sulphate, on a platinum wire, is put in a Bunsen flame the salt slowly evaporates and its vapor diffuses into the flame gases. The concentration of the vapor, except close to the bead, varies in the same way as the temperature due to a point source of heat at rest in a medium moving with uniform velocity. By studying the distribution of the luminous vapor around the bead its coefficient of diffusion can be estimated. Such experiments have been done by A. Becker,[26]

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[24] C. W. Heaps, Phys. Rev. September (1920).

[25] H. A. Wilson Phil. Trans. R. S. **A192,** (1899).

[26] A. Becker, Heidelb. Akad. **A7,** (1911).

H. A. Wilson,[27] G. E. Davis[28] and F. J. Symon.[29] Table XII contains the results obtained.

TABLE XII. *Coefficients of diffusion of alkali metal vapors in flames.*

Metal	A. Becker	H. A. Wilson	G. E. Davis	F. J. Symon
Li	1.3	14.5	12.4, 9.7	—
Na	1.2	11.5	19.0, 16.4	13
K	—	4.7	11.1	5.8
Rb	—	4.4	11.7	—
Cs	—	4.4	8.4	—
Tl	0.8	—	—	—
Sr	1.0	—	—	—

These coefficients have been supposed to be those for the neutral metal atoms since the light is emitted by such atoms. However, the metal vapor contains electrons which diffuse much more rapidly than the metal atoms so that an electric field must be set up which holds back the electrons and accelerates the diffusion of the metal ions. The metal ions must therefore diffuse more rapidly than the neutral atoms but of course the ions continually form neutral atoms to that this action must cause an apparent diffusion of the neutral metal atoms. This may be the reason that the coefficients of diffusion are so large.

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[27] H. A. Wilson, Phil. Mag. (6) **24,** 118 (1912).
[28] S. E. Davis, Phys. Rev. (2) **24,** 383 (1924).
[29] F. J. Symon, Proc. Roy. Soc. Edinb. **46,** 15 (1925).