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THE MOBILITY OF NA+ IONS IN N_2 AND H_2 AS A FUNCTION OF TIME

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ABSTRACT

The mobilities of Na^+ ions from a Kunsman source have been measured in H_2 and N_2 using gases of considerable purity and time intervals ranging from 10^{-5} to 10^{-1} seconds. The method used was the Rutherford A.C. method using both sinusoidal and square wave form oscillations. With corrections for temperature and pressure included the method gives reduced absolute mobility constants for the ions good to about 10 percent. The results indicated three distinct classes of ions in H_2 and probably three in N_2. In H_2 there is a fast ion of mobility 17.5 cm/sec per volt/cm which is presumably the atom ion Na^+ which exists up to time intervals of 10^{-4} seconds. It then undergoes an abrupt transition to an ion of mobility of about 13.5 cm/sec per volt/cm whence, after some 10^{-3} seconds, it gradually transforms to the normal ion in H_2 which has an absolute mobility of 8.4 cm/sec. per volt/cm. The intermediate ion is presumably a single molecular addition product, (possibly water vapor) to the initial Na^+ atom ion which retains its charge. The final so called normal ion may result from a gradual growth of the ion cluster by further addition of molecules, or by a gradual interchange of one or two primarily attached molecules to molecules of impurity that are strongly attracted but less prevalent, gradually making a stable ion. In N_2 the initial ion observed up to 5×10^{-3} seconds has a mobility of 3.75 cm/sec. per volt /cm. and probably changes abruptly to an ion of about 3.0 cm/sec. per volt/cm at the end of the interval. At the end of about 10^{-2} seconds it has transformed to the normal positive ion of 1.6 cm/sec. per volt/cm mobility. The interpretation is similar to that suggested for H_2. The mobilities of 17.5 and 3.75 for Na^+ ions in H_2 and N_2 give the first opportunity to check the theoretical mobility equations since in these cases the nature of the ion is known. They show that the Langevin theory assuming forces of dielectric polarization of an inverse fifth power type yields values of the mobility that are about 20 to 40 percent too low. This result was to be expected since it seems unlikely that ordinary forces of dielectric polarization observed in weak homogeneous fields should be capable of extrapolation to the huge inhomogeneous fields existing within a molecular diameter or two of an ion. The amount of deviation is however gratifyingly small and should prove of value in extending the theory.

INTRODUCTION

IN THE many researches concerning the nature of gaseous ions little progress has been made in arriving at a definite conclusion as to the ultimate nature of the ion (i.e. whether it is a large cluster or a small ion)[1] under ordinary conditions. The work of Erikson[2] on the relatively abrupt change of mobility with age for positive ions in air and the work of the writer on mobilities in gaseous mixtures[1,3] have definitely indicated the preferential addition of some molecules to the already somewhat indefinite ion. In the latter work

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[1] L. B. Loeb, Phys. Rev. **32,** 81 (1928).

[2] H. A. Erikson, Phys. Rev. **20,** 117 (1922); **24,** 502 (1924); **33,** 403 (1929); **34,** 635 (1929.)

[3] L. B. Loeb, Proc. Nat. Acad. Sci. **15,** 146 (1929); Phys. Rev. **35,** 184 (1930).

this action was shown to be a specific function of the chemical nature of the gas and the sign of the charge on the ion. Beyond this no definite knowledge of the nature of the ion could be derived, for these measurements indicated only *changes* of an abrupt sort in the ion which affected its mobility. Both workers, however, inclined to the belief that as a whole the ion was a complex of relatively few molecules, 2 or 3 at best, and that much of the reduction of the mobility was due to the attractive forces between molecules and ions not resulting in cluster formation.

It is clear that little progress can be made by such investigations unless the nature of the molecule actually carrying the charge (i.e., the nucleus of the ion cluster) can be studied. Heretofore many studies[4] have been made to determine the effect of the mass of the ion on its mobility. These all depended on assumptions as to the nature of the *initially ionized* molecule or atom (which was assumed to have retained its charge throughout). However, among all the researches done on this subject only those using as initial ions the radioactive recoil atoms, *detected by radioactive methods* were of any significance, and even these were of doubtful value because of the unknown size of the radioactive cluster torn off by recoil. The reason for the doubtful value of these earlier experiments could not at that time have been forseen. In the meantime, the immense amount of data on the transfer of energy between activated, excited, metastable and ionized molecules and atoms with neutral molecules, which have accumulated in recent years makes it most improbable that an initially ionized molecule of any ordinary gas (ionized by x-rays, radioactive radiations or ultraviolet light) has retained the charge in the 10^7 or more impacts with neutral molecules which occur in the ordinary periods of mobility measurement. Thus it is clear that in studying mobilities even under the most favorable conditions we have been completely in the dark as to the nature of the charged carrier, which for example, in H_2 may be a large organic molecule of low ionizing potential that may have in its many impacts annexed several other propitious companions. That such must in reality be the case in probably all previous mobility work follows at once from the fact that the collision frequency of ions in a gas is of the order of 10^9 collisions per second, and that even in the purest gases a purity of one part in 10^6 is exceptional at atmospheric pressure, (usually it is more nearly one part in 10^4 or 10^5). Thus the ion in one-tenth of a second can encounter from 100 to 10^4 molecules of an active nature with which change of charge or attachment may take place.

It is clear that what is needed in an analysis of the ultimate nature of the ions and their behavior as well as a test of our mobility theories is an investigation of ionic mobilities with *ions of a known nature*. Thus the measurements needed must be of such a sort that these ions can retain their charge, and at the same time the mobilities of such ions must be studied over intervals of time such that in a reasonably pure gas their chance of attachment is small. Now the positive ions of the alkali metals have ionization potentials far below those of any common gaseous molecules or organic impurities. They

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[4] L. B. Loeb, Jour. Franklin Inst. **201,** 279 (1926). Gives summary of literature.

should thus be able to maintain their identity as the positively charged nucleus of positively charged aggregates indefinitely. Such ions are easily obtained in quantity from the Kunsman catalysts at a reasonably low temperature. To insure the fact that the ions have not picked up a molecule of impurity or formed a cluster such ions must have their mobilities measured in time intervals of the order of 10^{-4} or 10^{-5} seconds for gases which have a purity of better than one part in ten thousand. It was therefore planned to study mobilities of Na^+ ions from a Kunsman source using a high frequency alternating potential of square wave form and an alternating current method. The square wave form was desired so as to make the results as definite as possible. The gas initially chosen was H_2 since this gas is one of the easiest to purify of more reactive impurities and since the gas is least injurious for the Kunsman source.

The adaptability of the Kunsman sources to ion mobility work in N_2 and H_2 even up to atmospheric pressure was clearly shown at the outset of this work and the sodium catalyst kindly sent by Dr. Kunsman proved admirable for these experiments. The square wave form oscillator of a type originally designed by J. L. Bowman[5] and initially set up by J. E. McVay in this laboratory did not prove so satisfactory. Preliminary results obtained with such an oscillator were published in a letter to the Editor,[6] and are in fact substantially confirmed by later work (from $T=10^{-4}$ to 3×10^{-5}, $k=17$, $T=5\times10^{-4}$ to 10^{-4}, $k=12.6$, and above 5×10^{-4}, 10 or less). However, it is much to be doubted if any reliance can be placed on results obtained by this method as a more critical investigation has shown. Recourse was therefore had to a sinusoidal wave form which was adapted to this problem in several modifications. All results were in general agreement, the later techniques, however, being the only ones in which much faith could be placed. It fortunately turned out that the measurements in N_2 could largely be obtained by a high frequency commutator with far more satisfactory results.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Source

It was essential to have an equipotential Kunsman source which could be raised to such a temperature as to give a good ion emission (450° to 750°C) which at the same time did not give off too many vapors. A great deal of difficulty was encountered until a steatite stone insulating material called "Lavite" was found. This material when raw can be turned on a lathe threaded and drilled. It can then be baked to 1000°C for twenty-four hours and becomes an exceedingly hard material with relatively little shrinkage. With this as a base the heating element, a platinum spiral of 0.1 mm wire, was mounted between thin quartz plates, 0.1 mm thick and a thin sheet of platinum foil with catalyst already burnt on and reduced, was screwed over the open end of the mounting by the small brass nut. The assemblage is shown in Fig. 1 in cross section and is self explanatory. The diameter of the

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[5] J. L. Bowman, Phys. Rev. **24**, 31 (1924).

[6] L. B. Loeb, Phys. Rev. **36**, 152 (1930).

open face of the catalyst was about 8 mm. The leads of heavy nickel from the platinum and from the coil were secured to the top of the lavite plug by brass clamps not shown. The whole was mounted in the heavy brass upper plate of the chamber and insulated from it by a quartz centering ring. The coil was heated by a storage battery and controlled by a rheostat, these elements being housed in grounded conducting cases to avoid electrostatic effects. This arrangement had a capacity, with the battery in the circuit, of some 660 cm as shown by direct measurement. Such a capacity when thrown into a tuned circuit above 5000 cycles during measurement could throw the circuit out of resonance by a serious amount. This limited the scope of the measurements considerably. The currents required for heating the source to a proper temperature varied with the gas and slightly with the pressure of the gas. Currents from 5.8 to 6.2 amperes were required in H_2 for pressures from 1 cm H_2 to 76 cm. In N_2 currents of the order of 4.2 to 4.5 amperes were required for the same pressure range. The source was mounted as the upper plate of a parallel plate system (plate distance used being of the order of 1.6 cm with upper and lower plates 8 cm in diameter), the lower plate being connected with amber insulated leads to the electrometer circuit. The assemblage could be mounted, the plates rendered parallel and plate distance measured by cathetometer before placing in the chamber. The chamber was cleaned by the writer's standard technique[7] except that a concentrated $H_2SO_4-K_2Cr_2O_7$ cleaning solution replaced the acids previously used. The gases used were tank H_2 or N_2 which were passed over the wrtier's standard purifying train of red hot Cu powder, powdered NaOH, $CaCl_2$, P_2O_5 and liquid air. In essence the gases were therefore of the best purity obtainable with the metal chambers used and the results at lower frequencies were comparable with previous results of the writer[9] in H_2.

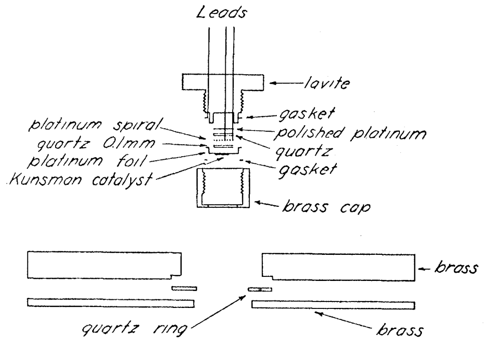

Fig. 1. Heater design.

The oscillators

A distrust of the wave form obtained from the Bowman oscillator as developed by McVay led the writer, on resuming the work in the autumn of

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[7] L. B. Loeb and A. M. Cravath, Jour. Opt. Soc. Am. and Rev. Sci. Inst. **16**, 192 (1928).

[9] L. B. Loeb, Proc. Nat. Acad. Sci., **12**, 617, 677 (1926).

1930, to a critical study of the method. In the earlier work on the oscillator the wave form had been determined by the Lissajou figure obtained in a cathode-ray tube oscillograph, the potential to be studied being placed on the one pair of plates, while oscillations of the same frequency and proper amplitude picked up from the oscillating system itself and so changed in phase by capacity as to be 90° out of phase with the oscillation to be studied were placed on the other pair of plates. The behavior of the Lissajou figures as capacity was varied on the latter system convinced the writer that a rectangular figure obtained in this fashion was not as significant as desired relative to the true wave form of the oscillations. Recourse was then had to the Beddell-Reich oscilloscope for a further study. This instrument proved to be fairly useful for indicating the wave form in the region from 1000 to 5000 cycles. A great deal of trouble was encountered with the stabilization above such frequencies since the stabilizing oscillations leaked through into the timing circuit and the time axis ceased to be linear. Another difficulty lay in the fact that except for the lower frequencies while the instrument served for a good visual study any tracing or record of the wave form for measurement was impossible due to lack of adequate stabilization without distortion with the power available.* However, with its use the circuit depicted in Fig. 2 was developed. In some cases the circuit was applied directly to the measuring chamber as shown by the connections in Fig. 3, or the same connections were made across R_2 on the first stage amplifier. The detailed description of this system will not be given, the figures and the data in the legend being sufficient. In working out this system several months were spent and a large variety of

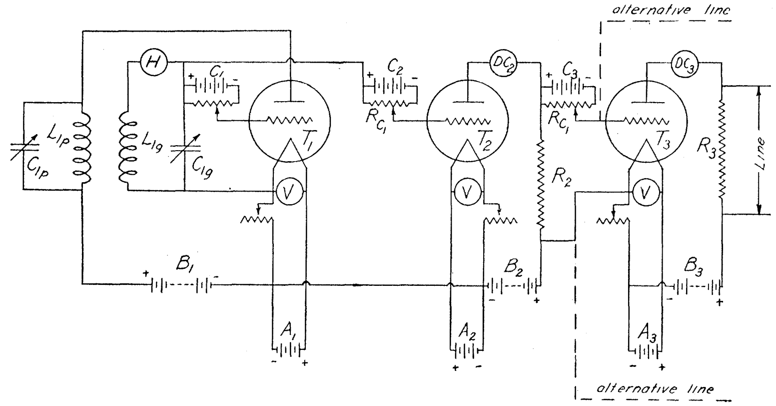

Fig. 2. Square wave form oscillator; T_1 and T_2 Radiotron UX 210 tubes. T_3 Radiotron UX 250 tubes. L_{1p} and L_{1g} Pacent honeycomb coils of appropriate inductance from 1500 turns to 500 turns. C_{1p} and C_{1g} either small radio condensers or glass condensers from 0.01 to 0.001 microfarad with 2 variable air condensers in parallel. $B_1=300$ volts. $B_2=300$ volts. $B_3=200$–400 volts. $C_1=27$ volts. $C_2=15$ to 40 volts as conditions altered. R_2 and $R_3=10{,}000$ ohms. $C_3=10$–30 volts, usually small.

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* Recently the writer has seen a very successful type of cathode ray oscillograph with a beautiful linear time axis up to 10^5 or more cycles built on the basis of improved argon rectifiers developed by Drs. Lauriston Marshall and Van Voorhis at Princeton. With these tubes it is possible that much progress can be made.

circuits tried. It will be noted that the potential of the oscillations as appled to the circuit varied from 0 to $-V_S$, while by means of a variable contact on a battery the 0 value was raised to a potential V_R above ground. V_S was always greater than $2V_R$ to keep ions from "working" across the plates. In the earlier work the ground was on the negative side and V_R was a retarding potential, the driving potential on the ions being $V_S - V_R$ and V_R being greater than $V_S - V_R$. Both methods worked equally well, the former being more convenient. A large number of measurements were made with this method in H_2. These measurements served to show that in general the ionic velocity was proportional to the field strength. The results were, however, inexplicably capricious until an oscillographic study revealed that the irregular behavior was caused by the fact that for each frequency used the value of the bias potential $C_2R_{C_1}$ was quite critical in that over-biassing made the upper half of the wave narrower than the lower half or vice versa. Since the mobility is computed for a uniform square wave by the equation $k = Nd^2/V_R$, where N is the number of half-cycles per second, (assumed equal), an inequality in the duration of the half-cycle results in a serious error. By working at the lower frequencies the oscilloscope showed when approximate equality of the upper and lower halves of the cycle was reached. Under these conditions the oscillations led to consistent values of the mobility. At higher frequencies this oscilloscopic study ceased to be possible and the square waves were abandoned. As this method of measuring mobilities indicated proportionality between ion velocity and field strength the square wave form was not considered essential and recourse was had to the more certain and accurate sinusoidal oscillations.

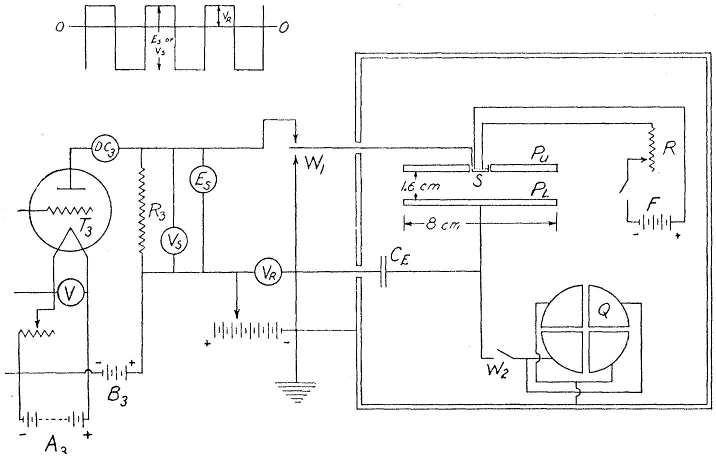

Fig. 3. Electrical arrangements for measurement: V_S = Kelvin multicellular voltmeter with capacity in series range 40–170 volts. E_S electrometer heterostatically connected for square waves. V_R = Hartmann-Brown d.c. voltmeter. W_1 = Switch for grounding or connecting ion sources to oscillations. S = source. P_U and P_L upper and lower plates. R = filament resistance, F filament battery electrostatically screened. C_E = grounding condenser to plate system, capacity 300 cm. W_2 = electrometer switch.

Sinusoidal oscillations of sufficient accuracy could be taken directly from the oscillator as in Fig. 4. In this case the amplitude of the oscillations cannot be varied without altering the frequency. While such oscillations may not be pure sinusoidal waves they have the advantage of steadiness and charging up the capacity of the ion chamber without throwing the system out of resonance as the ion chamber is cut in or out. This method was therefore the only possible one to use for the highest frequencies with existing capacities. Instead of varying the amplitude of the oscillations, the ground bias was varied by the bias battery V_R (Fig. 4) in such a fashion that that the field acting on the ions in each positive half-cycle could be increased or decreased. Since the distance the ions move depends on the area under the curve of the positive loop of the cycle multiplied by the mobility and divided by the plate distance,

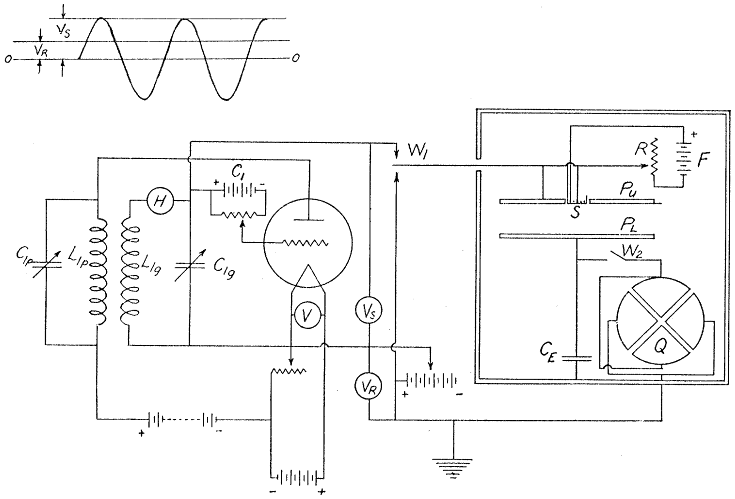

Fig. 4. Oscillator directly connected to measuring chamber, V_R variable. Symbols are similar to those in Fig. 2 and 3.

and as this area is varied by changing the bias V_R, this bias can be changed until the ions just cease to cross for the value of the product time times field strength contained under the positive loop as biassed.

Call V_S the root mean square value of the alternating sinusoidal potential call the mobility of the ion k, and let a and b be the intercepts of the sine curve with the line due to the bias potential V_R, then if T be the period of oscillation and d the plate distance, the ions will cross if

$$d = (2)^{1/2}\frac{V_S}{d}k\int_{a/\omega}^{b/\omega}\sin\omega t\,dt - \int_{a/\omega}^{b/\omega}k\frac{V_R}{d}\,dt$$

If $\theta=\omega t$, $dt=d\theta/\omega$ and $\omega=2\pi/T$ we have

$$\frac{2\pi d^2}{(2)^{1/2}V_STk} = \int_a^b \sin\theta\,d\theta - \frac{V_R}{(2)^{1/2}\,V_S}\int_a^b d\theta.$$

Calling $V_R/(2)^{1/2}V_S = A$ integration gives

$$\frac{2\pi d^2}{(2)^{1/2}kTV_S} = 2\cos(\sin^{-1}A) - A[\pi - 2\sin^{-1}]A$$

The right hand member of the equation, designated by ϵ, may be calculated as a function of A and plotted. Then

$$k = \frac{(2)^{1/2}\pi d^2}{V_S T\epsilon} = \frac{(2)^{1/2}\pi N d^2}{\epsilon V_S},$$

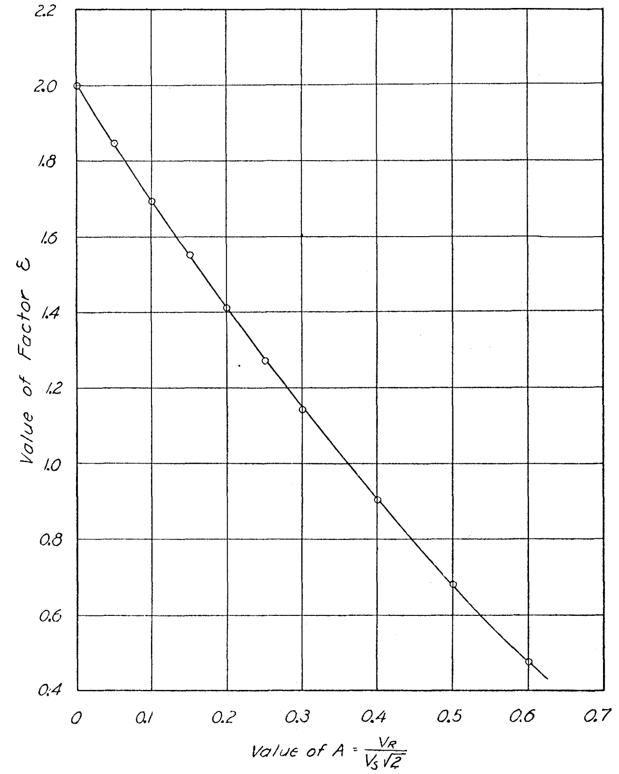

Fig. 5. Curve of ϵ against A.

where N is the frequency and ϵ is taken from the curve of Fig. 5 for the value of A corresponding to the ratio $V_{R_0}/(2)^{1/2}V_S = A$ obtained from the observed static voltmeter reading and the value of V_{R_0} for which the ions just cease to cross the distance d between the plates. A measurement using the oscillator directly is then achieved by keeping V_S constant and raising V_R until the ion current stops. If the oscillations are not accurately sinusoidal it is best not to have $V_{R_0}/(2)^{1/2}V_S$ too large as this accentuates the errors, which are most effective in changing the peak of the curve. Certain results obtained in the H_2 measurements shown in figure 12 are marked with question marks for just this reason.

To be more certain of the wave form other measurements were made with the oscillator and the first stage amplifier generating current in a coil L_2 coupled to a coil L_3 of the resonance circuit $L_3C_{R3}H$ in Fig. 6. The current in L_3 was varied by varying the potential B_2 in the amplifier. Hence the potential could be changed in $L_3C_{R3}H$ without changing the frequency. $L_3C_{R3}H$ was tuned with V_R and the plate system in the circuit (i.e. under the conditions of actual measurement).

With this arrangement either the potential across the static voltmeter system $C_V V_S$ could be kept constant and V_R changed to V_{R0} at which ions ceased to cross, or V_R could be set at 20–30 volts and the potential across $C_V V_S$ varied by varying the current in R_2 by means of the potential of the battery B_2. This latter method while by all odds the surest was most tedious and time consuming due to the slow period and low damping of the Kelvin multicellular static voltmeter used. An electrometer with rectifier used heterostatically served as a convenient voltmeter for rapid adjustment of the potential, but was not reliable within 1-2 volts in 100 for some unknown reason, generally reading a bit low. The slower method of measurement served to heat the gas unnecessarily and also to increase contamination.

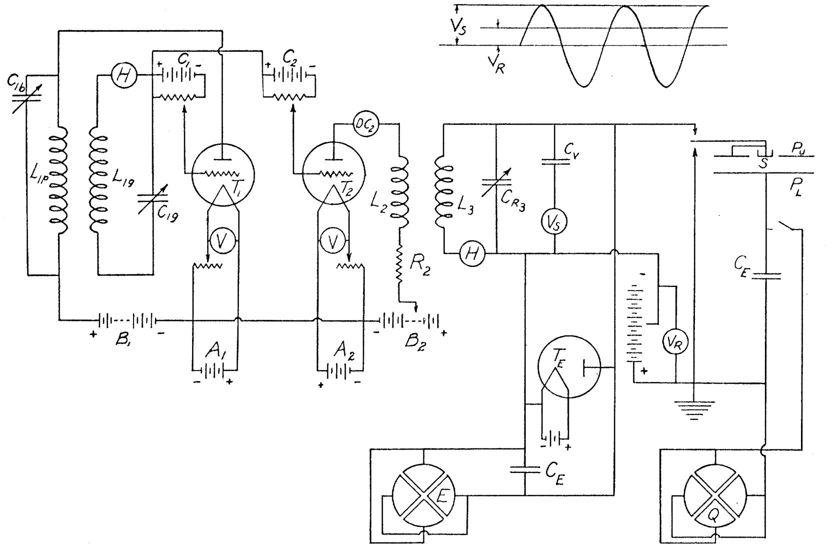

Fig. 6. Arrangement for tuned sinusoidal oscillations. L_2 = inductance in amplifier circuit coupled to L_3 in resonance circuit. C_{R3} = variable condenser in resonance circuit to tune it to the oscillating circuit. In general C_{R3} was kept as small as possible relative to L_3. E, T_E and C_E = electrometer rectifying circuit to measure the peak voltage of the oscillations. C_E = 0.002 microfarads. T_E = radiotron UX 299 tube.

Finally it was found that many of the measurements could be made by a square wave form commutator having 60 segments and capable of being rotated at 3600 r.p.m. With two auxiliary commutators and a series of gear ratios frequencies of alternation from about 5 per second to 3600 alternations per second of quite definitely square wave form could be obtained. The measurements with commutator and oscillator where they overlapped agreed quite satisfactorily.

The frequencies of oscillation were measured for the oscillator from 500 to 10,000 cycles by means of a beat frequency oscillator made by the General Radio Company of Cambridge, Mass., and above 10,000 cycles by a precision wave meter of the same firm.

Measurements

The general procedure of measurement was to evacuate the ionization chamber to from 3 to 5 microns and then run in fresh H_2 or N_2 over hot copper, NaOH, $CaCl_2$, P_2O_5 and liquid air in the writer's standard purifying train.[9] The pressure was then measured on a standard barometer as well as on the McLeod gauge if low, and the filament current turned on at a specified time. The oscillator or commutator had been set at a given frequency and steadied down, the frequency being measured before and after the run. To make a reading the alternating potential was measured with the ion chamber in the circuit. The chamber was disconnected from the alternating source, electrometer disconnected and the alternations again applied to the chamber across the plates and through the condenser C_E. After 10 seconds the oscilla-

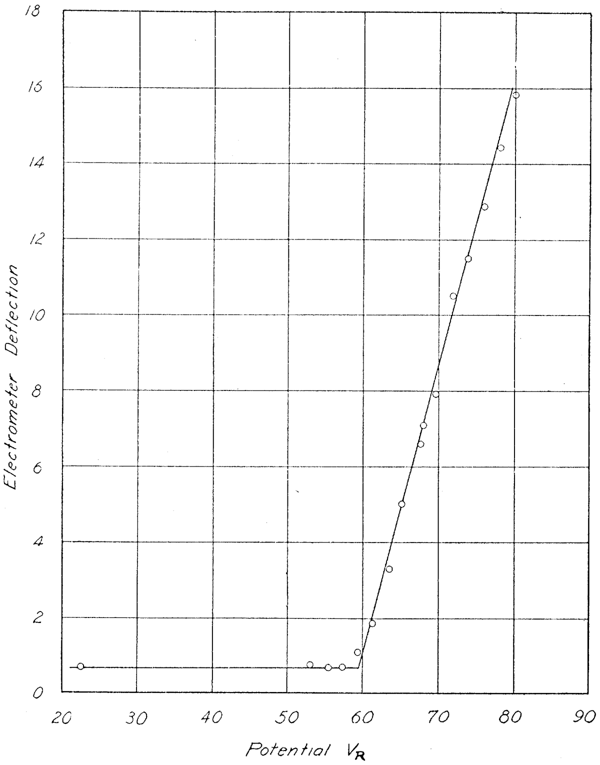

Fig. 7 Square waves, positive half-cycle less than negative half-cycle in ratio of about 1 to 1.3, using first stage and amplifier only. Pressure = 1.60 cm. Frequency = 6900 cycles. Mobility = 12.1. Hydrogen gas.

tions were cut off, the ground removed from the electrometer and electrometer connected to the collecting plate for 15 seconds (to control a small zero current due to space charge of positive ions) contact broken to the electrometer and the electrometer deflection noted. The sensitivity of the electrometer was 1500 mm per volt and the capacity of the electrometer system was some 350 cm. A series of values of currents were obtained for different values of V_S or V_R as the case might be, going up and down in potential around the region of the break point of the mobility curve. The temperature of the source usually increased with time, and this rendered the emission of Na^+ ions variable in time. As at rule, however, the current and temperature of the source steaded down after 20 minutes and reliable readings could be obtained over intervals of 20 minutes. It was undesirable to heat the gas any longer than necessary to obtain a curve on account of the temperature corrections, and also to avoid undue contamination of the gas. The measurements in general rarely lasted over 40 minutes. Occasionally two runs were made on the same sample of gas, but in most cases gas used for more than 1 hour was replaced by freshly purified gas. Pressures were read again at the end of a run and the change in pressure gave a good indication of the rise in temperature of the gas as a whole. In N_2 it was 8° in 30 minutes at 65 cm and in H_2 it was 10° in 40 minutes at the same pressure.

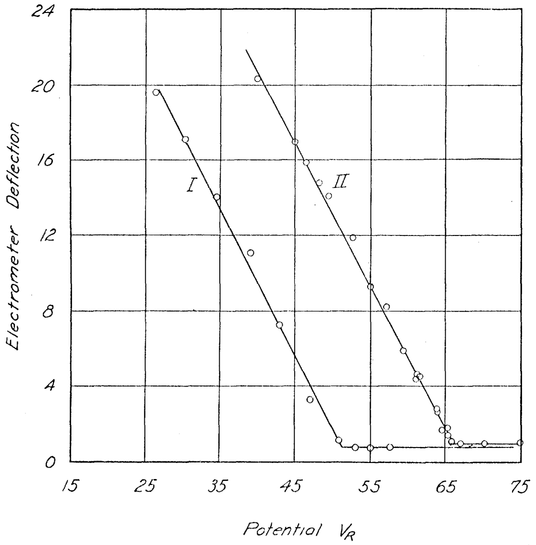

Fig. 8. Sinusoidal oscillations in hydrogen gas. Curve I from oscillator direct, varying retard bias potential V_R. Pressure$=0.51$ cm. Frequency$=38{,}000$ cycles. $V_S=124$ volts, $V_{R_0}=51.3$ volts. $\epsilon=1.117$. $K=19.7$ cm/sec per volt/cm. Curve II from tuned circuit activated by current from primary amplifier, varying retard bias potential V_R. Pressure$=1.61$ cm. Frequency$=20{,}250$ cycles. $V_S=172.5$ volts. $V_{R_0}=66$ volts. $\epsilon=1.22$. $K=22.9$ cm/sec per volt/cm.

Typical current-potential curves obtained by the various methods outlined above are shown in Figs. 7, 8, 9 and 10 for which details are given in the legend. Fig. 7 was taken with the square wave form oscillator using only the first stage amplifier. The frequency was 6900 cycles but the positive half-cycle was distinctly narrower than the negative half-cycle as viewed in the oscilloscope. Hence the calculated mobility was 12.1. If the mobility be increased by the estimated ratio of the width of the upper and lower half-cycles as seen in the fleeting glimpses in the oscilloscope the mobility should have been 1.3×12.1 or about 15.7 cm/sec, a value more or less in agreement with other values for the intermediate ion. The current potential curve it is seen is nearly linear and the break point is sharply defined. Fig. 8 has two curves both obtained using sinusoidal oscillations of constant amplitude V_S in which the bias potential V_R was varied. Curve I used the direct sinusoidal oscillations from the oscillator while curve II used the oscillations in the resonance circuit. The break points are again sharp and these ions are the very fastest ions in H_2 (i.e. those that have not had an opportunity to age). Figs. 9 and 10 show curves obtained with a square wave form commutator. Fig. 9 is for N_2+10 percent H_2 showing the intermediate ion, while Fig. 10 is for H_2 at 61 cm pressure. Both these indicate asymptotic feet due to transformation of ions while in the measuring field, those in H_2 being particularly pronounced. To estimate the intercepts in the curves of Figs. 7 and 8 is simple.

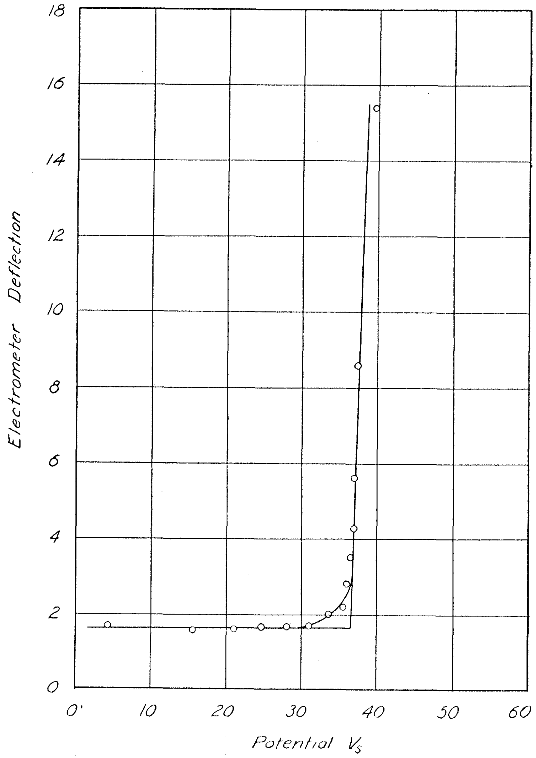

Fig. 9. Square waves from commutator in nitrogen with 10 percent hydrogen. Six segment commutator, gear ratio 1:1. Pressure = 2.03. cm. Frequency = 900 cycles/sec. Mobility = 3.58 cm/sec per volt/cm.

In the case of Figs. 9 and 10 the estimate of an extrapolated break point in the curves for the linear portions of the curves would seem to be the only proper procedure.

Interpretation of current-potential curves

The extrapolation raises the question of just what such curves signify, and what the break point means. With radioactive or other ion sources where saturation currents are easily obtained the shape of the mobility curve relative to the saturation curve enables a great deal to be determined about the ionic constituents present.[10] In the present case with a thermionic ion source such a study was impossible. The curves give the average velocities of those ion groups which *first* cross the electrode distance *d*. If ions of one mobility only are present then since the geometry of the system is quite regular the ions liberated first in the phase should get across at a very definite potential and a nearly linear increase of current should follow in the early portion of the curve. If two ions of widely different mobilities are present one might anticipate precisely the type of curves and transitions which appear for negative ions in air from 15 to 5 cm pressure using a photoelectric source.[11] The resolving power of the present method is, however, relatively low and differences

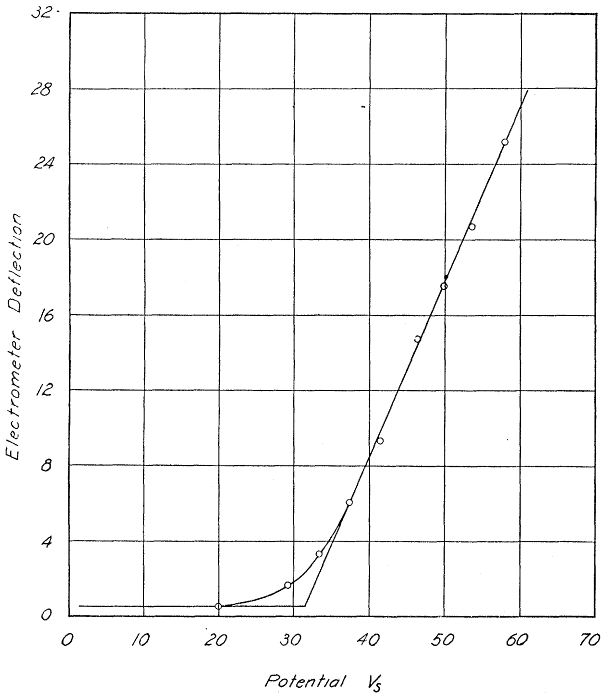

Fig. 10. Square waves from commutator in hydrogen. Pressure = 61.42 cm. Frequency = 78 cycles/sec. Mobility = 8.6 cm/sec per volt/cm, the value for normal ions.

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[10] L. B. Loeb, Jour. Franklin Inst. **196,** 537, 771 (1923).

[11] L. B. Loeb, Phys. Rev. **17,** 89 (1921); Jour. Franklin Inst. **197,** 45 (1923).

of 30 percent in mobility would with the positive ion sources used never be clearly resolved as two separate groups. Where ions of two mobilities are present, one of which changes to the other, in a time interval compariable with the time of crossing, the statistical nature of the transformation will result in a sort of hybrid current-potential curve representing the averge velocities of the ions with an asymptotic foot and an intercept for the lower nearly straight portion of the curve giving an intermediate value of the mobility. Such curves are readily deduced from theory for a statistical type of attachment.[11] The end of the asymptotic portion may or may not represent the fastest ion present, as it depends only on the sensitivity of the instruments and how nearly complete the transformation is in the time of measurement (i.e. on the number of ions crossing without transformation). Hence, assuming that in general only one type of ion is relatively stable after a given number of impacts in a gas due to impurities present; and thus that the time of transition is relatively short, one would expect the intercepts of the curves to be sharp where single stable groups are concerned giving constant mobilities, but asymptotic in time intervals covering the transformation process, and with the uncertainty of the saturation value giving, as extrapolated above, intermediate values of the mobility.

Where there may be several successive transformations with but a small difference in mobility of the ions formed the method of study used should yield a continuous series of mobilities as the time of observation, and hence the transformation, progresses. These should eventually approach some limiting stable value, namely that for the so-called normal ions in the gas. The method is thus capable of giving mobilities for the relatively stable ions, and indicating a succession of changes with time occurring where individual average mobilities are numerous in the regions where transformations occur, or where the ions are *not* clearly differentiated. It will be noted that in fact the results obtained are such as to be in complete accord with this discussion, a circumstances which will be discussed later in more detail.

Temperature correction

Before the final results obtained and their interpretation can be discussed, a final correction to be applied must be discussed. The mobility is measured in a chamber at constant pressure. As the mobility in the ordinary ranges of temperature is at constant density little affected by temperature, little account need be taken of the changes in temperature of the gas as a whole. However, the source of ions is at a temperature ranging from a very dull red heat to a rather bright cherry red (i.e. from about 500° to 750°C) while the lower plate is at the temperature of the heavy brass case of the ionization chamber. The upper plate which is electrically equipotential with the hot source may attain some 200°C towards the end of a measurement. Thus, a temperature gradient exists in the 1.6 cm of gas in the gap where the mobility is measured, which is a maximum in precisely the region where the ions are being studied. As the pressure is constant the gas density in the ion path varies inversely as the absolute temperature, and hence the mobility obtained is higher in the ratio of the average absolute temperature than it would be computed from the initial conditions in the chamber. All mobilities must therefore be reduced in proportion to the ratio of initial temperature at which the pressure was measured to the average temperature in the gas path. This correction was exceedingly difficult to obtain inasmuch as experimental conditions preclude computations, though the energy input into the heating element for N_2 and H_2 enabled the relative conduction by the gas and by the metal to be determined. One estimate of the average temperature in the gap was achieved by measuring the mobility of the ions at atmospheric pressures with relatively impure gases and comparing the observed (assumed normal) mobility with those for normal ions in the gases. This method was used as an ultimate check on the temperature correction more directly determined. After mobilities had been measured the chamber was opened and six copper-constantan silver soldered thermocouples of No. 38 wire mounted on a thin mica leaf were placed along the axis of the upper and lower plates between them. The distances of the couples from the source were accurately measured by cathetometer and temperatures were measured in the gap as a function of time and at different gas pressures, with varying currents in the filament, corresponding to the currents actually used in measurement.

The temperature study showed that the temperatures given by the couples rose to a nearly steady condition within 5 minutes after the source was brought to temperature, it being customary gradually to raise the filament up to full current. Thereafter the temperatures changed relatively slowly at most 40°C an hour at the couple 1 mm from the source and 25° an hour at the lower plate. Changes in pressure made relatively little change in the couple temperatures, the temperatures being slightly lower for the same source temperature at higher pressures. The temperatures read on the couples for H_2 are shown plotted against distance from the source for the various couples in Fig. 11 in curve I. This curve is far from a linear gradient such as a convectionless gas should show under the conditions of 8 cm pressure with 1.6 cm plate distance, the upper plate being heated. The interpretation that the radiation from the source raised the gas-cooled couples above the gas temperature is obvious. Since the couples cool more rapidly than the gas by metallic conduction and radiation an estimate of the gas temperatures was made as follows. The filament was suddenly cut out and a series of timed readings of the temperatures in the gap were made. The measurements revealed that in less than 3 minutes in H_2 the couples had dropped to a linear gradient and thereupon the whole curve gradually fell at a somewhat more rapid rate than its rise after the first five minutes after turning on the current. The linear curve in H_2 is shown in Fig. 11, curve II, and gives an average gap temperature of 80°C, the room temperature being 22°C. In N_2 the temperatures were not quite as high, and the time to reach a linear gradient for the couples was longer. The average temperature was slightly lower for N_2 in all cases. The gradients were lower at pressures above 20 cm while the heating current required to give the same temperatures of the source was higher. This indicated some convection in the gas at these pressures. In view of the relatively small variation in the average temperatures observed it was decided to correct the H_2 mobilities for 80° (or reduce them by a factor of 295/375 to give the true values), while for N_2 the average temperature of 55° was used and the correction factor was 295/350. The values yielded by these correction factors at atmospheric pressure gave mobilities in accord with the normal absolute mobilities to be expected of gases from this method, to wit about 8.6 cm/sec per volt/cm for H_2 and 1.6 cm/sec per volt/cm for N_2 within the certainty on these measurements. In any case it was clear that the above temperature correction, while if in error might change the absolute values by possibly 10 percent, it would not seriously impair the value of the otherwise striking results.

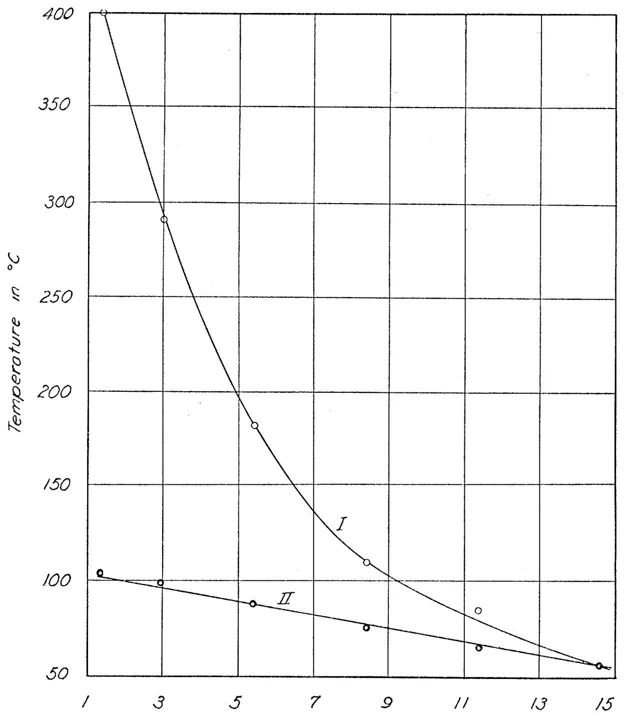

Fig. 11. Temperature gradient by thermocouples in H_2. Pressure 7 cm. I. Filament on. II. Filament off 40–60 seconds later.

Other than the density correction above, which also entailed a correction of the mobility for the initial gas pressure, no other correction was needed to deduce the mobility constant for the ions (i.e., the reduced mobility). The use of the inverse density law (law of Langevin) is justified in this case by wide experience and the recent results of Tyndall and Powell.[21] It was also verified in many of the present measurements. A very minute correction could have been made for the fall of potential across the auxiliary condenser C_E, it was however too small to include compared to the other uncertainties.

In conclusion therefore it may be stated that the results obtained measure a sort of average mobility of Na^+ ions in H_2 and N_2 for the faster ions present at any time. Where only one stable class of ions is present at the time we obtain absolute values of the mobility by this method good to better than 10 percent.

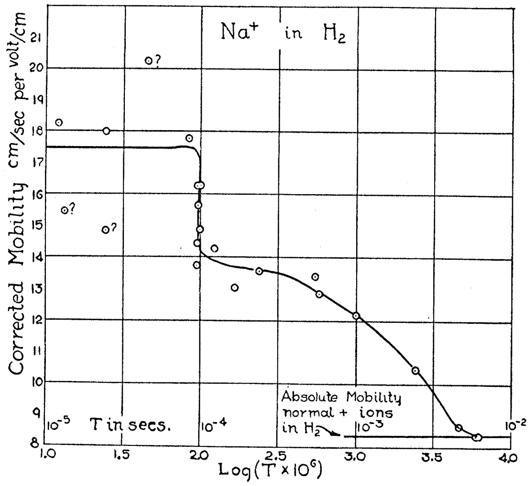

Fig. 12.

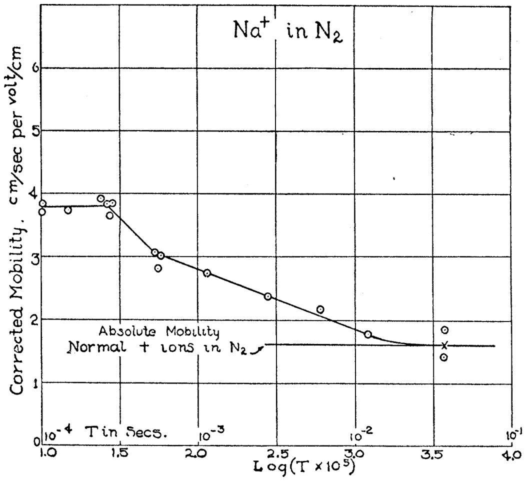

Fig. 13.

RESULTS

The results for the two gases H_2 and N_2 may be summarized by the curves shown for H_2 and N_2 respectively in Figs. 12 and 13. In these figures the reduced mobility constants are plotted against the logarithm to the base 10 of the time necessary for the ions to cross, i.e., the time of a square wave form oscillation or the half period of a sinusoidal oscillation. The two times are not exactly equivalent, but for the present purposes they suffice. The plots on this scale have the effect of telescoping the results obtained over slightly different times together and accentuate the abruptness of the transitions. It is seen that both of the sets of curves agree in general outline. Within 10^{-4} seconds for H_2 and 5×10^{-4} seconds for N_2 or less, the ions have very high mobilities, around 17.5 cm/sec per volt/cm in H_2 and 3.7 cm/sec per volt/cm in N_2. At the end of these time intervals there is a more or less abrupt change in mobility to a stable ion of mobility 13.5 cm/sec in H_2 and about 3 cm/sec in N_2. The stability of the N_2 ion is not as clearly indicated as in the case of the H_2 ion owing to the impossibility of observing the mobility at intermediate time intervals with the commutator. After these time intervals both gases show a more gradual change in mobility with time, reaching eventually the so called normal value of the mobility usually encountered in these gases. This normal value is *not that usually given but is the real absolute standard of mobility for normal positive ions in these gases*, which have been indicated by Loeb,[10] Tyndall[12] and Grindley, and lately confirmed by Bradbury.[13] The abrupt change in mobility in H_2 is perhaps exaggerated by the action of impurity and possible variations in the ion path temperature. Different degrees of purity of the gas (time of sojourn or heating in the chamber, etc.) at this point had a marked effect on the mobility. On either side of this point, however, the purity made relatively little difference. The points with question marks attached to them were those taken with conditions that made absolute values doubtful, hence the value chosen for the mobility of the fastest ion in H_2 may be in error by as much as 5 or possibly 10 percent.

The facts are, however, quite definite that there are at least 3 different mobilities for a charged atom ion Na^+ in H_2 and probably as many in N_2. The first and fastest ions exist for lengths of time of 10^{-4} seconds in H_2 and 2×10^{-4} seconds in N_2. The second class of ions exist from 10^{-4} to 10^{-3} seconds in H_2, and possibly from 2×10^{-4} to 10^{-3} seconds in N_2, and the last class are the so-called normal ions in H_2 and N_2 measured above 10^{-2} seconds in relatively pure H_2 and above 10^{-2} to 10^{-1} seconds in relatively pure N_2.

Discussion of Results

From the fact that the Na^+ ion will retain its charge the following conclusion can be drawn concerning the first and fastest ion. The ions make on the order of 10^9 collisions with molecules per second. Granted a possible gaseous purity of one part in 10^4 molecules of these gases (a not unreasonable assumption) one can estimate that in H_2 in 10^{-4} seconds the ions can on the average meet but 10 or possibly less molecules of impurity. If on the average one in two collisions with such impurity molecules causes attachment of such molecules to the ion, then at the end of 10^{-4} seconds a goodly share of the Na^+ ions will have added one molecule. That the molecules attaching to the Na^+ ion to decrease its mobility must be impurity and not N_2 or H_2 molecules follows at once from the 10^5 impacts needed to attach and from the mixture work.[1] The sharpness of the drop also indicates that the process is probably

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[12] Tyndall and Grindley, Proc. Roy. Soc. **A110**, 346 (1926); Phil. Mag. **48**,**711** (1924).

[13] N. E. Bradbury, Phys. Rev. **37**, 1311 (1931).

the addition of a single molecule. Since we are measuring the fastest ions that cross in appreciably numbers, the downward parts of the curves of Figs. 12 and 13 represent an interval in which most of the ions have attached impurities. In N_2 the conditions are analogous, there being possibly less impurity than in H_2. What the impurity is one cannot say, but the probable contamination in these cases would most likely be water vapor, probably driven out from the heating element by the heating. Since the values assumed above seem reasonable, one may conclude that the chance of the faster ions in H_2 themselves being complex is unlikely. One may thus assume with considerable assurance that the ion of mobility of 17.5 cm/sec in H_2 represents the mobility of the Na^+ atom in ion in H_2. In N_2 the frequency was not pushed beyond 10^4 cycles and it may be that the Na^+ ion in pure N_2 has a still higher mobility than the value of 3.8 cm/sec noted. Further work is in progress to determine this. The significance of the actual values will later be discussed in connection with ion theories.

The second class of ion in both gases, then, as time goes on appears to alter its mobility in such a fashion that the separate steps are not clearly resolved. The behavior could be taken to indicate the formation of several intermediate stages of the clustering process, in which separate ions do not differ greatly in mobility (i.e., the addition of 1, 2 and 3 more molecules of some impurity to the first stage addition product), finally reaching some rather stable limiting size. Such an explanation would infer a rather complicated cluster ion of 4 or more molecules. On the other hand the subsequent steps might as simply be explained by assuming that the ions later pick up all sorts of molecules of heterogeneous character (some hydrocarbons of assorted character, etc.) which are present as still rarer impurities. Thus in this region of change the ions are quite heterogeneous in average mobility and the mobilities observed as time passes take on all sorts of progressively lower intermediate values. Eventually in some 10^{-2} seconds all ions have had an opportunity of rearranging themselves in harmony with their environment so that they are more or less uniform in structure, most ions having eventually only added one or two molecules of a relatively rare impurity, but one having a selectively high electrochemical affinity for a positive charge and giving the most stable ion. Such behavior would yield what we term normal ions, which have a more or less uniform mobility. The two processes outlined would then lead to a normal ion of nearly unique mobility, either by adding so many molecules that in more than 10^{-2} seconds the average constitution is the same (a molecule more or less little changing the ionic mobility) or else by interchanging its constitution so frequently that eventually the ions achieve a uniform composition as the addition product of some rarer but more strongly attracted molecules. As to which process is the true one, mobility measurements cannot at present say, though the writer is inclined to favor the latter process.

There is unfortunately not a single method whose resolving power is sufficient to answer the important question which is raised by these experiments as to the uniformity of the mobilities over a relatively large range. Some writers[14,15] purport to fine separate *classes* of ions of various velocities among normal ions. In no carefully controlled observations by the majority of the observers using the most diverse methods has this conclusion ever been verified. There have, however, been a large number of observations where the width of the velocity spectrum peaks observed in mobility measurements makes the question of a continuous distribution of mobilities within narrow limits among normal ions possible. In this group belong Erkison's,[16] La Porte's,[17] Zeleny's,[18] Van de Graaf's,[19] Tyndall[20] and Grindley's, and Bradbury's[13] observations, which owing to the nature of the methods leave much to be desired as regards resolving power. The recent admirable work of Tyndall and Powell[21] also raises the same question. The writer is inclined to believe that the width of the peaks of the latter are due to the dispersion of the ions through the use of the gauzes whose interpenetrating fields cause just such effects, as the writer[10] has shown. The writer is inclined to believe on the basis of measurements made in air using the simple Rutherford A. C. method on negative ions[10] that the close agreement in shape of the mobility-saturation ratio plotted against field strength, with the theoretical mobility curve based on the assumption of a single ion of definite mobility can only be reconciled with that assumption. Here again the question of resolving power is raised and it may well be that mobilities may be spread over a considerable range. Until this question is settled it is futile to go much further in speculating as to the nature of the second stage in the formation of the normal ion.

If an analogy to the second step in the formation of the ions is to be looked for in previous results it is probable that it might correspond to the change in mobility of positive ions with age observed by Erikson,[2,16] which is most interestingly influenced by water vapor and purity. However, the faster form of the positive ion in this case has a higher mobility than Erikson's and the change in mobility observed in these gases is more gradual. This later difference could be ascribed to the probable greater purity of the gases used (less impurities and hence a longer average transition period) and also to the fact that in this method the faster ions are always measured and hence the faster ions are measured in part in the longer time intervals, while Erikson measures the time for the average ion to transform. In addition the contaminations from ionization in Erikson's measurements were different from those encountered here which could in part account for the difference.

[14] J. J. Nolan, Proc. Roy. Irish Acad. **33,** 9 (1916); **36A,** 74 (1923); Phys. Rev. **24,** 16 (1924); also **25,** 101 (1925); Phil. Mag. **1,** 417 (1926).

[15] Haines, Phil. Mag. **30,** (1915).

[16] Erikson, Phys. Rev. **20,** 117 (1922).

[17] La Porte, Ann. de Physique **8,** 466 (1927).

[18] John Zeleny, Phys. Rev. **31,** 1114 (1928); **34,** 310 (1929); **36,** 35 (1930).

[19] Van de Graaf, Phil. Mag. **6,** 210 (1928).

[20] Tyndall and Grindley, Proc. Roy. Soc. **A110,** 346 (1926).

[21] Tyndall and Powell, Proc. Roy. Soc. **A129,** 162 (1930).

Theorectical Considerations

The fastest Na^+ ions in H_2 and N_2 if correctly interpreted as representing the mobility of the atom ion of sodium in these gases make possible the first real test of the existing mobility equations. Of the various equations developed two perhaps should be drawn on to compare with observations. One of these is the elastic solid ion theory of Langevin[22] which represents a good equation of this type. While questioned by Lenard and Mayer[23] it still furnishes an adequate basis for rough comparison though it may be deficient in details. This theory assumes an ion and molecule, the half of the sum of whose diameters is σ and whose charge does not affect its means free path. Since σ can be determined approximately from the radii of Na^+ ion and H_2 and N_2 molecules, as estimated from kinetic theory, the mobility can be easily computed from the Langevin equation that

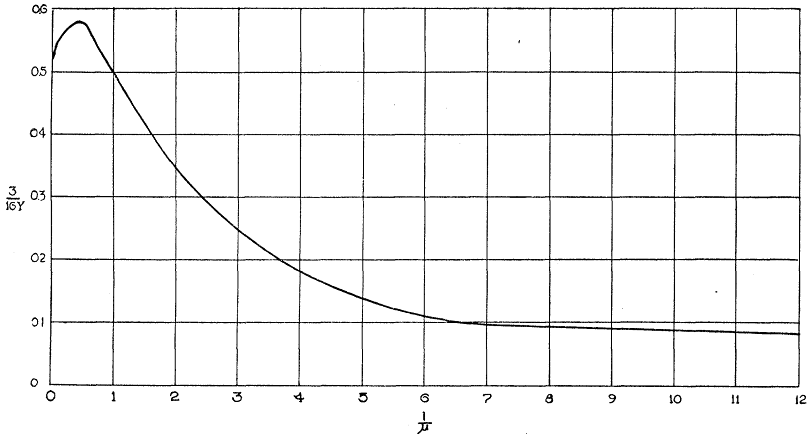

Fig. 14.

$$k = 0.815(e/M)(\lambda/C)((M+m)/m)^{1/2}$$

where e is the charge, M the mass of the gas molecules, $\lambda = 1/\pi\sigma^2 N$, C the velocity of thermal agitation of the gas molecules, N = the Loschmidt number, and m is the mass of the ion. The most plausible of all ion mobility equations is, however, the full Langevin[24] equation assuming elastic-solid ions and molecules but including an attractive force between ion and molecule of the form $f = (D-1)e^2/2\pi N\sigma^5$; that is an inverse fifth power law of attraction based on the di-electric polarization of the molecule by the charge on the ion, where D is the dielectric constant of the gas. This has been verified mathematically in recent years by Hasse[25] and again carefully verified on the basis of its assumptions by H. A. Kramers at the writer's request in connection with another problem. The equation reads

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[22] P. Langevin, Ann. Chim. Phys. **28,** 317, 495 (1903).
[23] H. F. Mayer, Ann. d. Physik **62,** 358 (1920).
[24] P. Langevin, Ann. Chim. Phys. **8,** 238 (1905).
[25] R. Hasse, Phil. Mag. **1,** 139 (1926).

$$k = \frac{3}{16Y}\,\frac{0.465}{\frac{\rho}{\rho_0}(D-1)_0M_0)^{1/2}}\left(\frac{M+m}{m}\right)^{1/2}$$

where $3/16Y$ can be evaluated by the curve of Fig. 14 as a function of $1/\mu$, where μ is

$$\left(\frac{3(D-1)_0e^2}{4\pi N\sigma^4MC^2}\right)^{1/2}.$$

ρ and ρ_0 are the densities of the gas at any pressure and temperature and that at N.T.P., $(D-1)_0$ is the value of $D-1$ at N.T.P. and M_0 is the molecular weight of the gas. The relation between $3/16Y$ and $1/\mu$ is given by the curve shown in Fig. 14 and follows from the elastic solid impacts and the ratio of potential and kinetic energies of the ions and molecules. It assumes that the *dielectric polarization follows the inverse fifth power law to distances between centers of ion and molecule comparable with the quantity* σ. It happens that the factor $3/16Y$ for the Na^+ ions in H_2 and N_2 has a value nearly 0.505. In Table I are given the values of the mobilities computed on the two theories and the observed values for the mobilities of Na^+ in H_2, and Na^+ in N_2.

TABLE I.

	Langevin solid elastic	Observed	Langevin inverse fifth power law
Na^+ in H_2	48.7	17.5	10.25
Na^+ in N_2	14.9	3.75	2.72

The observed results it is seen fall in between the theoretical values, being far lower than the neglect of the electrical forces would lead one to expect, and yet larger than results to be expected from a consideration of the usual dielectric forces as well as solid elastic impacts. The conclusions to be drawn are very simple and should have been predicted. It is obvious that the dielectric forces must play some role so that the elastic solid theory falls very wide of its aim. On the other hand, the writer[4,26] has oftentimes pointed out that we have no right to assume that the value of the forces due to dielectric polarization at the point where the forces in this work are most important (i.e. at distances of the order of σ) are the same that one would get for forces of dielectric polarization produced in a weak uniform force field. In other words, when one gets to fields of the order of magnitude of that at 3×10^{-8} cm from a charge of 4.77×10^{-10} e.s.u. which are non-uniform fields of the order of 1.6×10^{8} volts/cm and less over the neutral molecules, the molecules and atoms are so distorted that the ordinary dielectric polarization can no longer be assumed to apply. Hence the law of force assumed, $(D-1)e^2/2\pi Nr^5$, is not strictly applicable in this region. One might venture to guess that under these conditions the forces must increase less rapidly as the distance r between ion

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[26] L. B. Loeb, Kinetic Theory of Gases, McGraw-Hill, New York, 1927, p. 477; Phys. Rev. **32,** 81 (1928).

and molecule decreases. The result will be that the computed mobility would be higher than that computed above on the ordinary law of force. These results thus give us for the first time a definite indication of the order of magnitude of the deviations caused by the acknowledged deficiency in our best ion theory. Kramers also pointed out to the writer that the repulsive forces should be treated not as elastic solid forces but as repulsive forces of the type recently handled by the wave mechanics in the case of molecular interaction. It is likely that such a correction would have the effect of reducing the sharp maximum of the curve of Fig. 14. Whether the advances in the study of the molecular forces of distortion and repulsion by the wave mechanics will at this time make it possible to carry the analysis of Langevin further in line with these indications is doubtful. However, it is to be hoped that in the future the problem may be successfully solved, and the results above appear most suggestive in this connection.

In conclusion the writer wishes to express his gratitude to his friend and associate, Commander Telesio Lucci, of the Italian Navy, retired, Assistant in Physics at the University of California, for his invaluable assistance throughout the tedious course of these investigations.