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THE MECHANISM OF THE TRIBO EFFECT

by

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NOTE: The work on the mechanism of the tribo effect is completed. Therefore, this special report is also intended to serve as the final report on the subject.

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Abstract

Electrification in friction has been studied quantitatively. Glass balls roll through a glass tube and fall into a Faraday cage. The individual charges on 150-200 balls are recorded and evaluated statistically. Primary variables are rate f of feed of balls into the tube ($f = 1$ to $f = 70$ balls per minute) and time τ spent by each ball in the tube (inclination of tube $\alpha = 2^\circ$ to $\alpha = 29^\circ$). The empirical formulae obtained for the average absolute charge q and the fraction of positive balls N_+ are $q = k_2 \tau \sqrt{f}$ and $N_+ = k_4 \tau^2 \sqrt{f}$. The atmosphere in the tube is the ambient. Blowing O_2 through the tube makes $N_+ = 0$ and increases q by a factor of 2.5. Blowing N_2 through the tube has no appreciable effect.

The mechanism of charge generation has been identified as to its main features. Friction causes disturbance of the equilibrium between the glass surface and the atmosphere and reactions tending to restore this equilibrium and to establish equilibrium between the two surfaces in contact. These reactions are oxidation - reduction reactions. Instrumental in charge transfer are H and OH, products of H_2O.

1. INTRODUCTION

When two bodies of different insulating materials are rubbed against each other, they become electrostatically charged, one positively, the other negatively. When the two bodies are of the same material, they do not acquire charge. It was reported by Shaw[1], however, that when two rods of ebonite are rubbed against each other while held perpendicularly to each other, i.e., such that one, the rubber, is rubbed at one spot while the other, the rubbed, is rubbed along its length, the rubber becomes first negative and the rubbed positive, but continued rubbing reverses the signs. In this experiment, the two rods are initially identical, but they become different as to surface area rubbed and amount of rubbing. It is well known that dust blown off the ground or, in general, powder rubbing against a solid body of the same material, acquires electrostatic charge. The net charge is close to zero, but the charges on the individual particles may have large positive and negative values. This case is materialized when a powder is sprayed through a metal nozzle because the metal becomes covered by the powder[2, 3].

Owing to the practical importance of the electrification in friction, e.g., fire hazard, the phenomenon has been studied extensively in the past More recently, the interest in aerosol's has initiated investigations. These investigations have produced information on charge distribution and the factors that influence amount and distribution of charge, but the mechanisms by which charge is generated and distributed have remained obscure. In order to obtain information on these mechanisms, quantitative measurements under controlled conditions are required. In particular, it is necessary to observe each particle individually and to determine its friction and its charge. This is hardly possible with a large number of particles as in a powder, and the information available is therefore essentially qualitative or semi-quantitative.

The experiment reported in this paper is designed to supply such quantitative information. It is inspired by the experiment by Shaw, just referred to. One may ask what Shaw's result would have been had he used a fresh rubber for each stroke. This case comes close to simulating a stream of powder particles rubbing along a tube. In our experiment, glass balls were rolled through a glass tube into a Faraday cage, and the charges acquired by the individual balls through friction against the tube were recorded.

The electrification of glass in friction has been studied extensively. Reference may be made to Vieweg[4)], who studied the effect of water after drying in a dessicator, and Rizzi[5)], who studied the effect of heating. The effect of surface treatment has been studied by Vieweg[4)], Shaw and Jex[6)], and Knoblauch[7)]. The results of these investigations are that water has a fundamental effect, and that the acid-base nature of surface contaminants in aqueous solution is decisive to sign and magnitude of charge. The effect of the atmosphere upon friction electrification has been studied by Jones[8)] and by Debeau[9)]. The latter investigator concluded that adsorption from the atmosphere constitutes the essence of the phenomena.

Clearly, friction does not create electricity, it merely causes a redistribution of electrical charge, i. e., transfer of electrons from one body to the other. The mechanism of electrification is thus related to that of electron transfer from a solid to an electrolyte or from a solid to a vacuum. The former case applies to friction in the ordinary atmosphere and, generally, in the presence of moisture. The mechanism of electron transfer from a metal electrode to an electrolyte is described by the formula [10)]

$$e_{metal} + H_2O_{sol} \longrightarrow H_{metal} + OH^-_{sol}$$

The electron transfer is thus effected by H_2O or, rather, by decomposing H_2O. The receiver of H becomes positive, and the receiver of OH becomes negative.

The transfer of electrons to a vacuum or a gas from a solid exposed to friction is known as the Kramer effect. This effect will not be discussed in this connection because the electron transfer to an electrolyte is more directly applicable to two solids separated by a film or water.

It follows from the evidence referred to that the essence of electrification in friction is the disturbance of the equilibrium between surface and atmosphere and subsequent reactions with the constituents of the atmosphere, particularly water, to restore this equilibrium. These surface reactions are similar to those on electrodes immersed in an electrolyte They cause electron transfer and thereby electrification. This view will be pursued in detail in Section 5.

In view of the essential role of the atmosphere, one would like to study electrification in different atmospheres. The apparatus used in our experiments permits study in the ambient atmosphere only It is hoped that the effect of the atmosphere will be studied quantitatively in a continuation of this investigation However, the data obtained in the ambient atmosphere permit conclusion on the main features of the mechanisms involved

2. EXPERIMENTAL APPARATUS

The experimental setup is shown in Figure 1. Glass balls are fed through the funnel and copper tube, to the right of Figure 1, into a glass tube and roll through the glass tube into a Faraday cage, to the left in Figure 1. The charges acquired by the balls through friction against the glass tube are recorded on an Esterline-Angus recorder together with the General Radio DC Amplifier. The funnel and copper tube are connected to ground. (This does not remove the charges from the balls,) and the glass balls are therefore charged when they enter the glass tube. The frequency f at which the glass balls are delivered into the glass tube is controlled by a shutter that is operated by a motor-driven cam With two motors of different gear ratios with two cams of 1 and 4 notches, and by varying the voltage on the motor, the frequency f can be varied continuously between 1 and 70 balls per minute.

The glass tube has an internal diameter of 10 mm and a length of 24 inches The glass balls have a diameter of 5 ± 0.5 mm. The tube is made of Pyrex glass, the balls of borosilicate glass

The inclination of the glass tube is measured by means of a protractor and a plumb line Four different inclinations were used 20.0°, 28 5°, 12.5°, and 2.1°, in this sequence.

Figure 1. Photograph of Apparatus Used in Study of Origin of Charge.

The input resistance of the amplifier is set at 10^{10} ohms. This gives almost complete discharge between the balls even at the highest frequency. Higher frequencies would require a smaller input resistance and a corresponding loss of accuracy. The voltage from the Faraday cage is of the order of volts and the charge on the ball of the order of up to 100$\mu\mu$C, depending upon the experimental conditions. The charges are measured and evaluated in terms of scale degrees, the absolute amount of charge being of no moment to the purpose of this investigation.

The Faraday cage consists of two coaxial cylinders as shown in Figure 2.

No means are available for the control of temperature and humidity in the room, but these quantities are recorded on a Serdex Hygrothermograph.

3. EXPERIMENTAL PROCEDURE

The glass balls and the glass tube were first tried as received from the supply house. Numerous exploratory runs were made while trying out the apparatus. Although these were not evaluated, they showed reproducibility of the main features. In particular, both positive and negative charges were recorded. After these runs and prior to quantitive studies, the balls were all cleaned in water under exposure to ultrasound. The effect of this treatment was studied later. However, after cleaning, the charges were negative with initially no positive charges at all. After numerous runs in connection with a modification of the feeding device, the initial state was qualitatively reproduced. The quantitative studies were then undertaken with the balls in this state.

Throughout the entire investigation, the balls were never touched by the hand. Balls spilled on the table or the floor were put aside. The balls were kept in a glass flask and poured into the funnel. They were recovered from the Faraday cage by pouring them back into the storage flask.

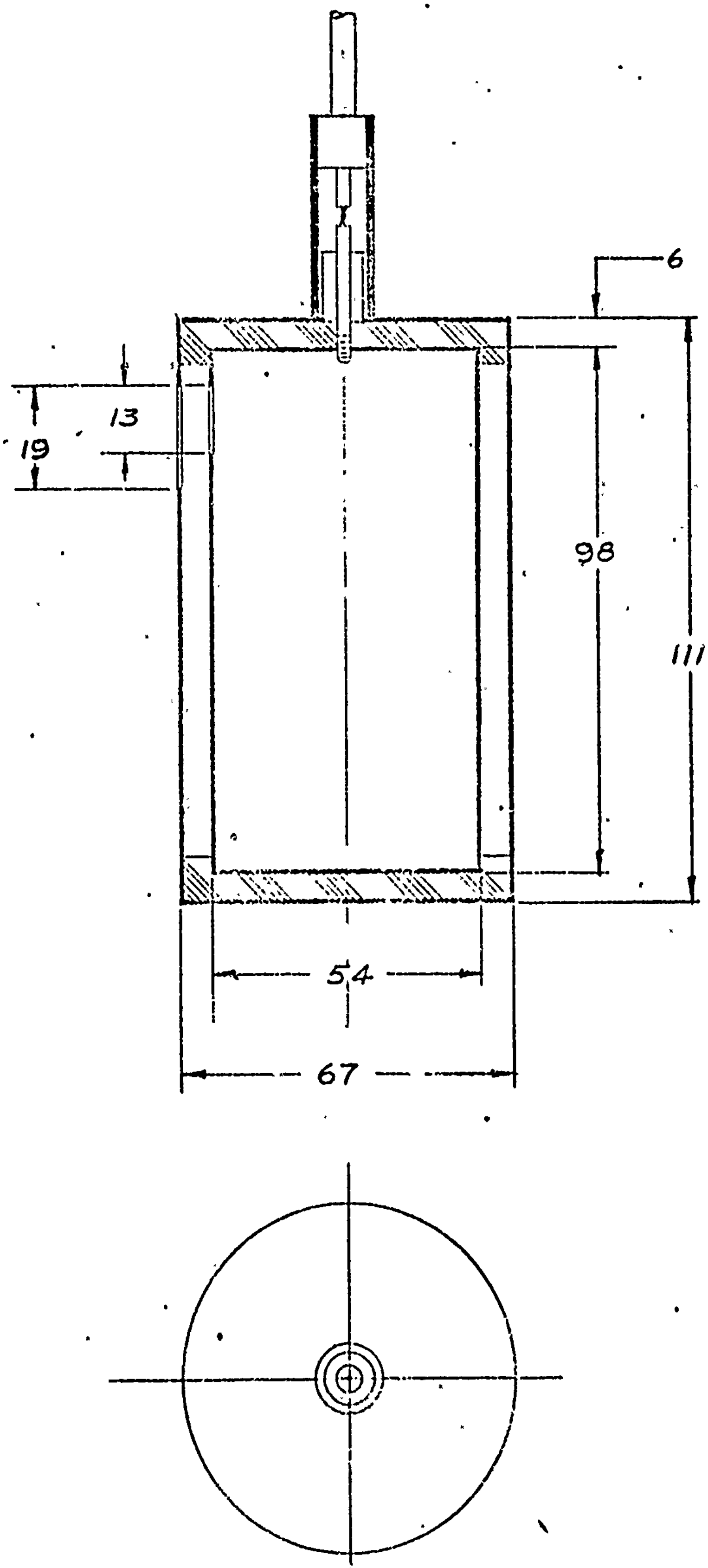

Figure 2. Faraday Cage (Dimensions in mm.)

The results were reproducible within the accuracy to be expected, and no trend in the data from repeated runs could be discerned. In runs at different frequencies, the frequency was altered in a random fashion in order to eliminate the effect of any change with time or wear upon the relation between charge and frequency. No such effect was noticed.

After completion of the study of the dependence of charge upon frequency of balls and inclination of tube, the effect of cleaning was studied. The balls were divided into three lots. Each lot was poured into an Erlenmeyer flask, distilled water was filled on, the water was boiled to expel air, and the flask was sealed. Each lot was then exposed to ultrasound for 10 minutes, one lot with O_2, one lot with N_2, and one lot with air bubbling through the water before and during exposure. The balls were dried under a light bulb, and the three lots were stored in separate flasks. These balls were then run separately and repeatedly over a period of 200 hours at two frequencies, 7 and 28 balls per minute, and at an inclination of 20.6^{o} in order to study the effects of aging and wear upon the charge.

When this study was completed, the balls cleaned by ultrasound under air were run 10 times, the same balls being used in all these runs, at a frequency of 28 balls per minute and an inclination of 20.6^{o}. This experiment was then repeated twice, each time with freshly cleaned balls, in a series of 13 consecutive runs.

After running the three lots of balls as just described they were boiled in water and the runs at 7 and 28 balls per minute, inclination 20.6^{o}, were repeated.

Finally, the balls cleaned in ultrasound under N_2 were cleaned again under air. These balls were then run at four frequencies 1, 4, 7, and 28 balls per minute, at an inclination of 20.6^{o}.

The apparatus does not permit experiments with a controlled atmosphere in the glass tube. However, two exploratory experiments were run with N_2 and O_2, respectively, blown through the glass tube from the entrance end.

4. EXPERIMENTAL RESULTS

4.1 "NORMAL" BALLS

A typical record is shown in Figure 3. The records were evaluated as to number of positive, negative, and neutral balls, charge distribution, and average positive, negative, absolute, and net charge. A typical charge distribution is shown in Figure 4. The other quantities determined are shown in Figures 5 - 11.

For "normal" balls, the average absolute charge is

$$q = k_1\sqrt{f} \tag{1}$$

as shown in Figure 5. The value of k_1 is

$$k_1 = k_2(\operatorname{cosec} \alpha)^{1/2} \tag{2}$$

as shown in Table 1 and Figure 6, α denoting the inclination of the tube. The relation (2) holds for $\alpha \geqq 12.5^\circ$. There is no increase in k_1, when α is reduced from 12.5° to 2.1°.

TABLE 1.

α	2.1°	12.5°	20.0°	28.5°
$\sin \alpha$	0.03664	0.21644	0.34202	0.47716
$\operatorname{cosec} \alpha$	27.290	4.6202	2.9238	2.0957
k_1	2.86	3.15	2.50	2.12
k_1^2	8.18	9.81	6.25	4.49
$k_1^2 \sin \alpha$	——	2.13	2.14	2.14
k_3	32.6	30.3	19.5	12.8
$k_3 \sin \alpha$	——	6.56	6.67	6.11

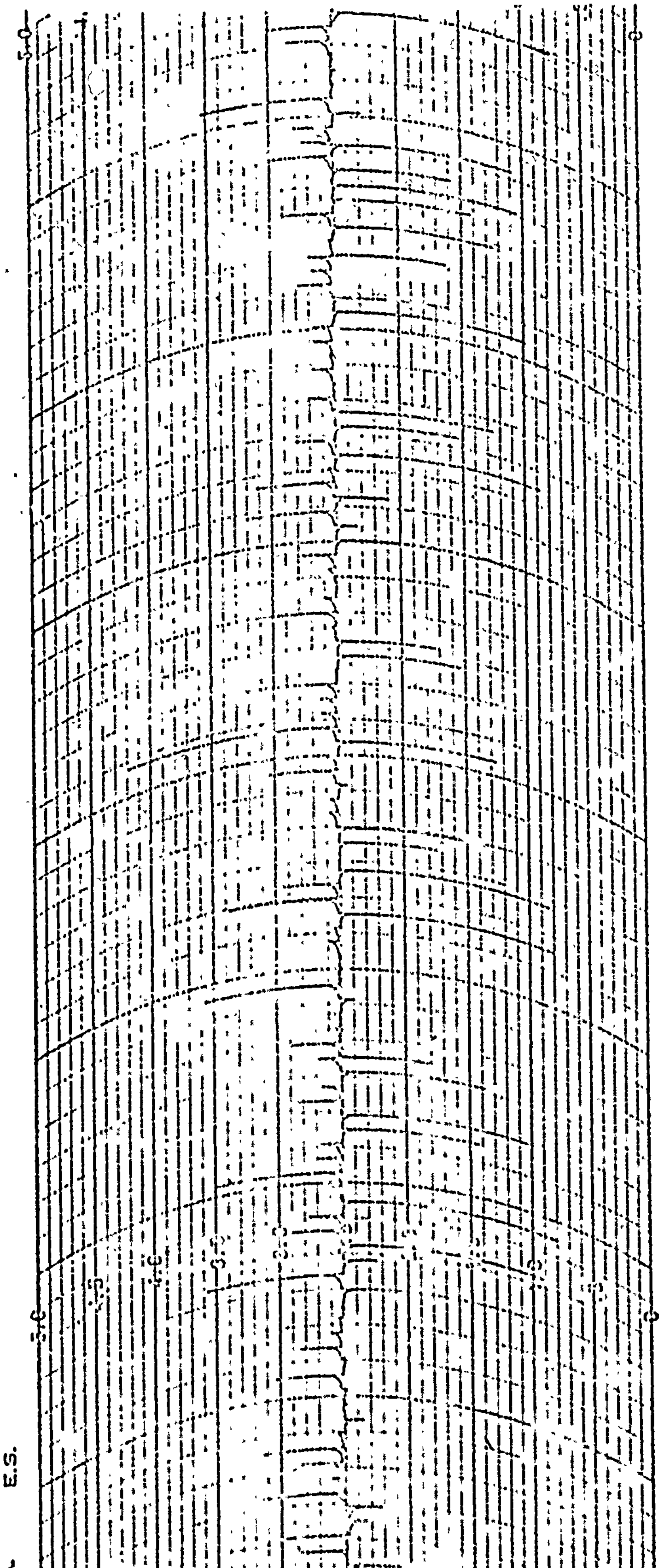

Figure 3. Typical Record of Charge of Individual Glass Balls.

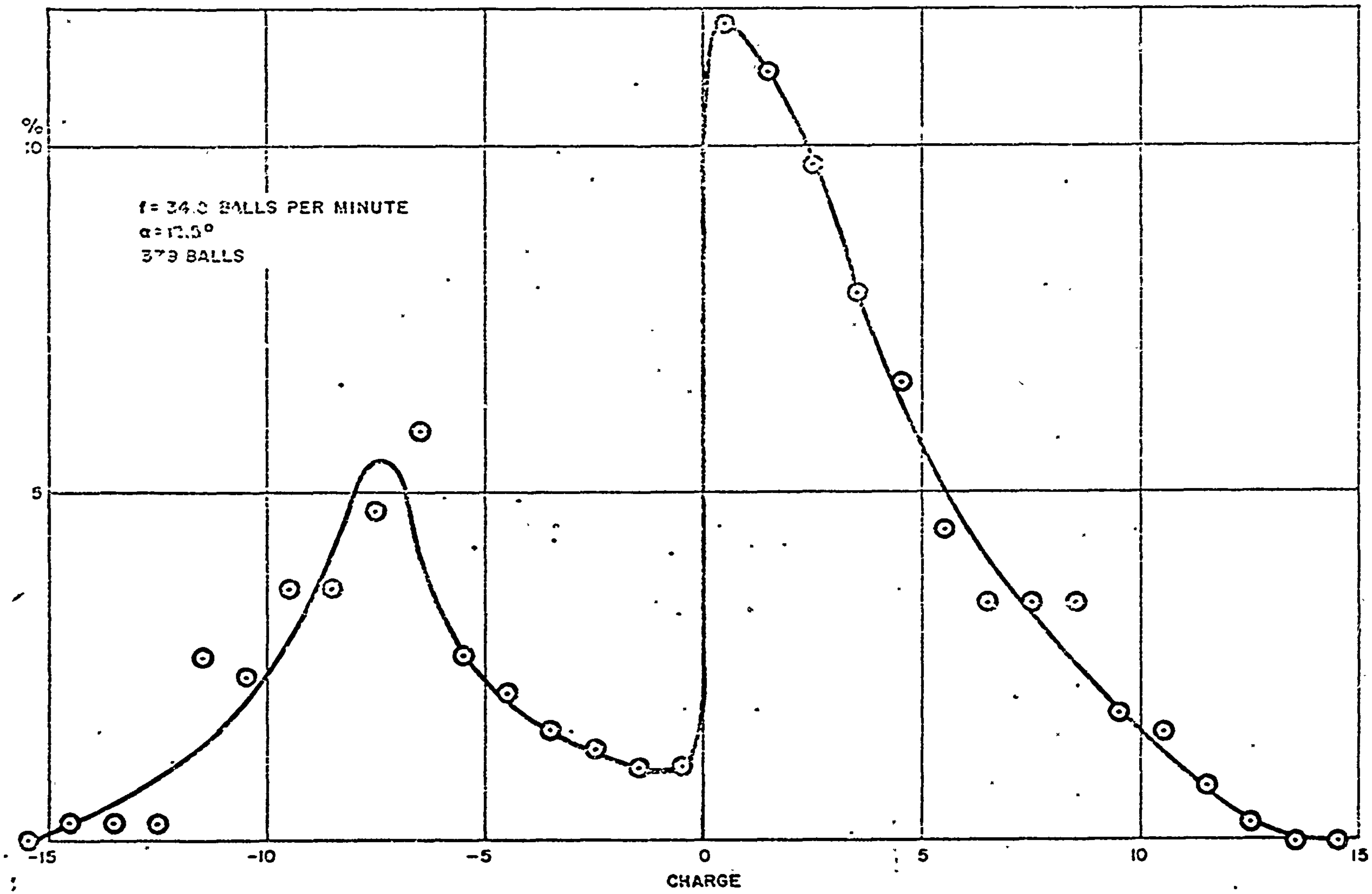

Figure 4. Typical Distribution of Charge on the Glass Balls.

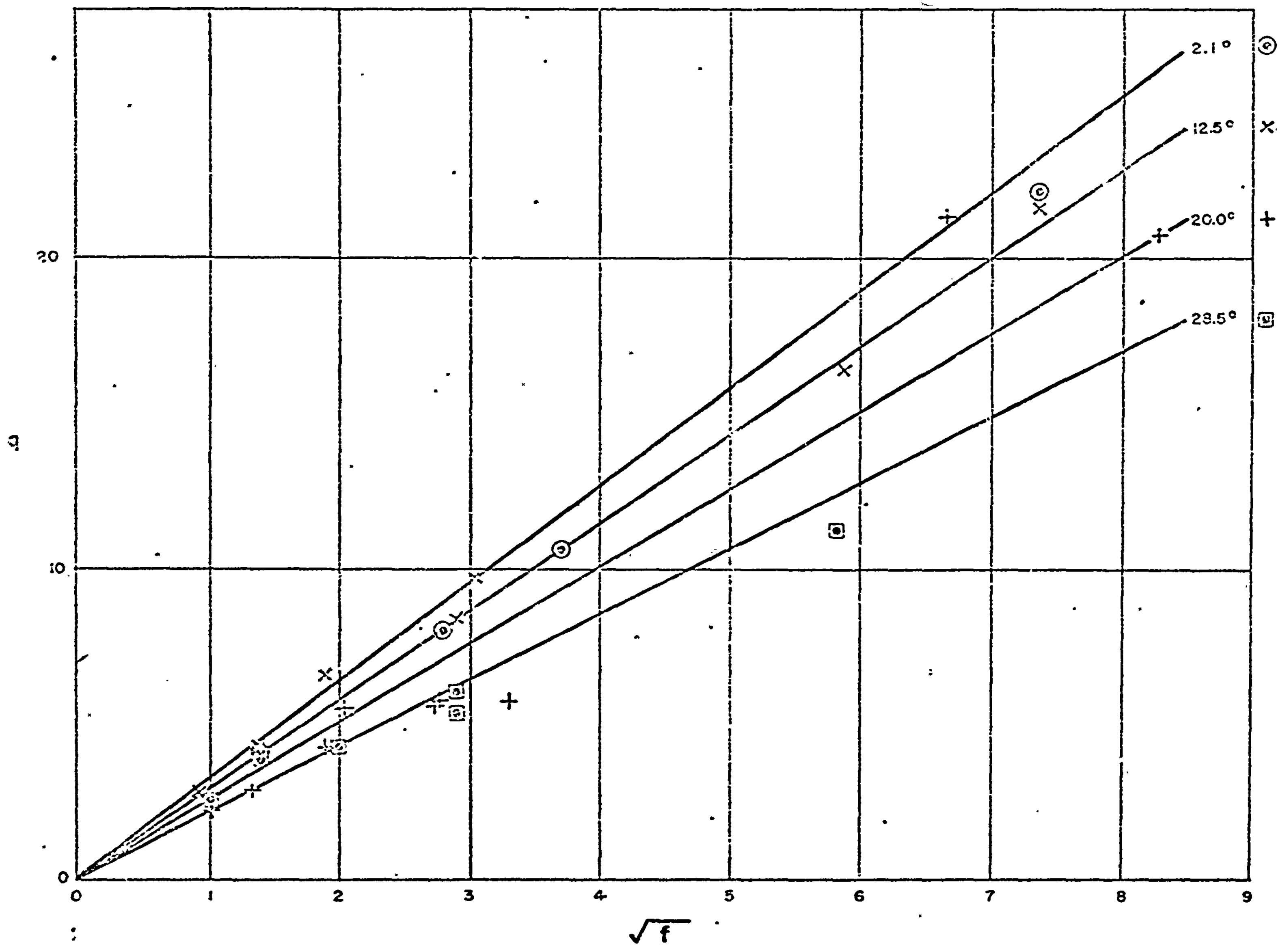

Figure 5. The Average Absolute Charge q on the Glass Balls as a Function of the Square Root of the Frequency f at Which the Glass Balls are Fed into the Glass Tube. . .

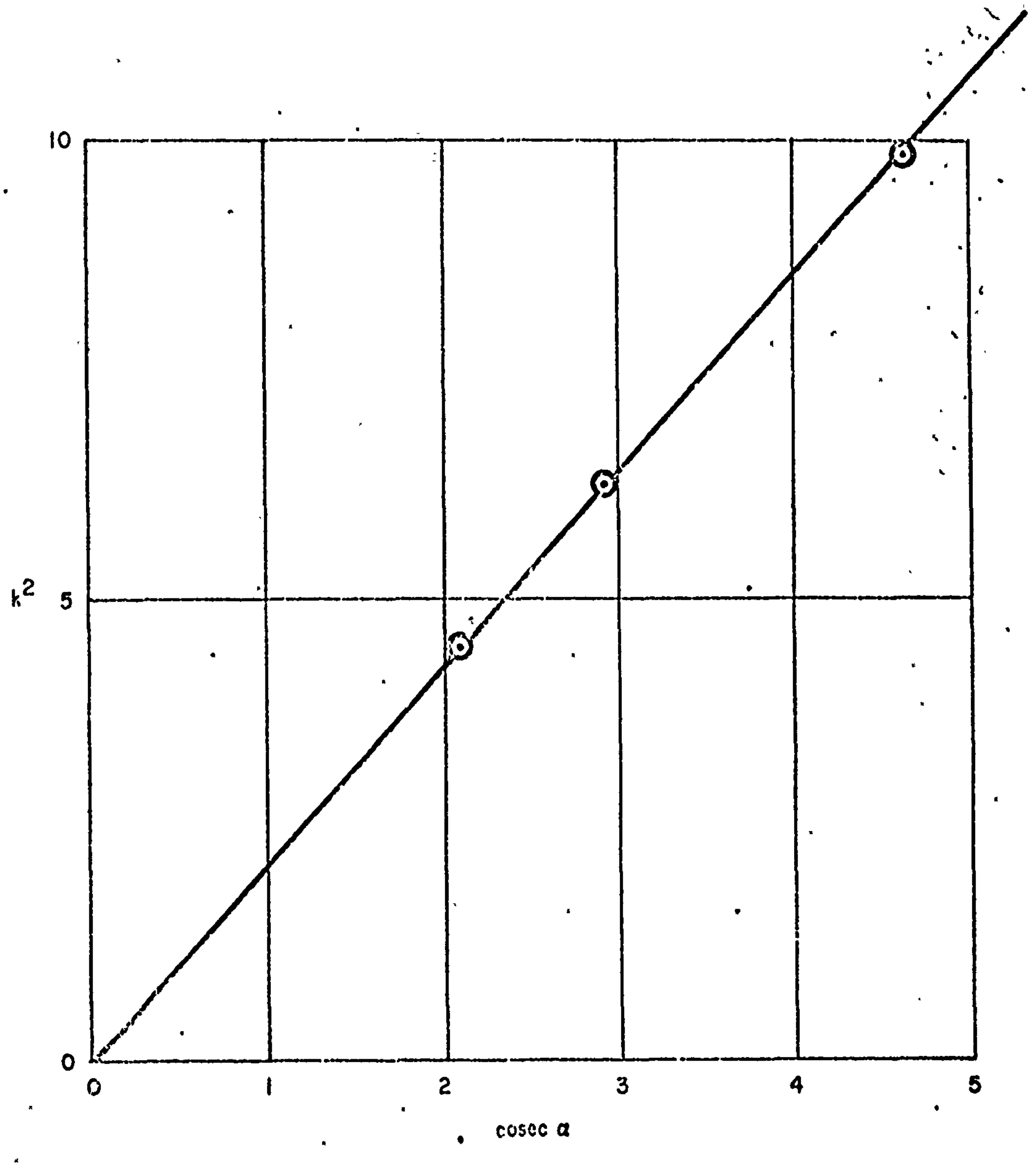

Figure 6. The Square of the Slope k_1 of the Lines in Figure 5 as a Function of cosec α, When α Denotes the Inclination of the Tube.

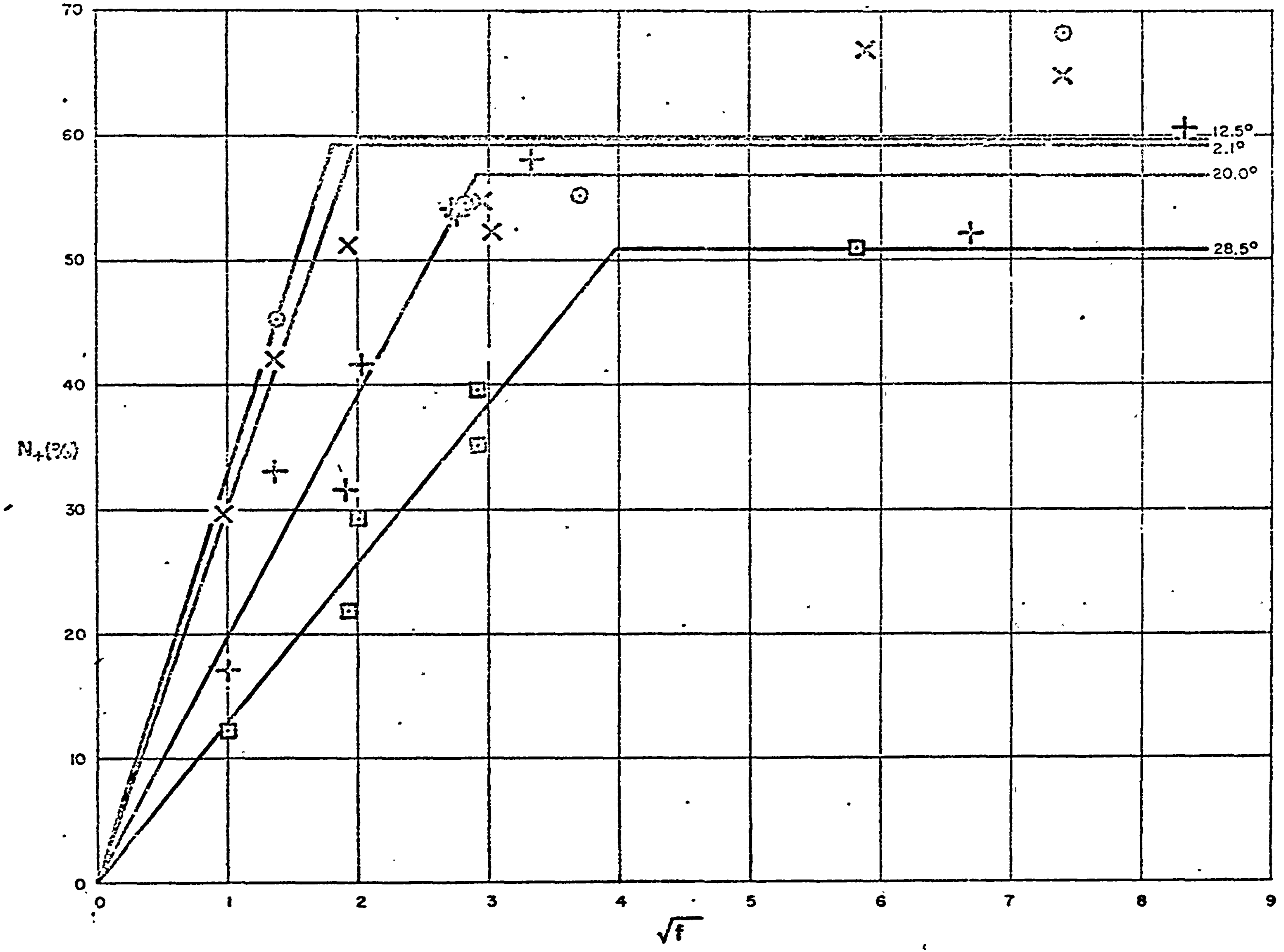

Figure 7. The Percentage of Positively Charged Glass Balls N_+ as a Function of $\sqrt{f}$.

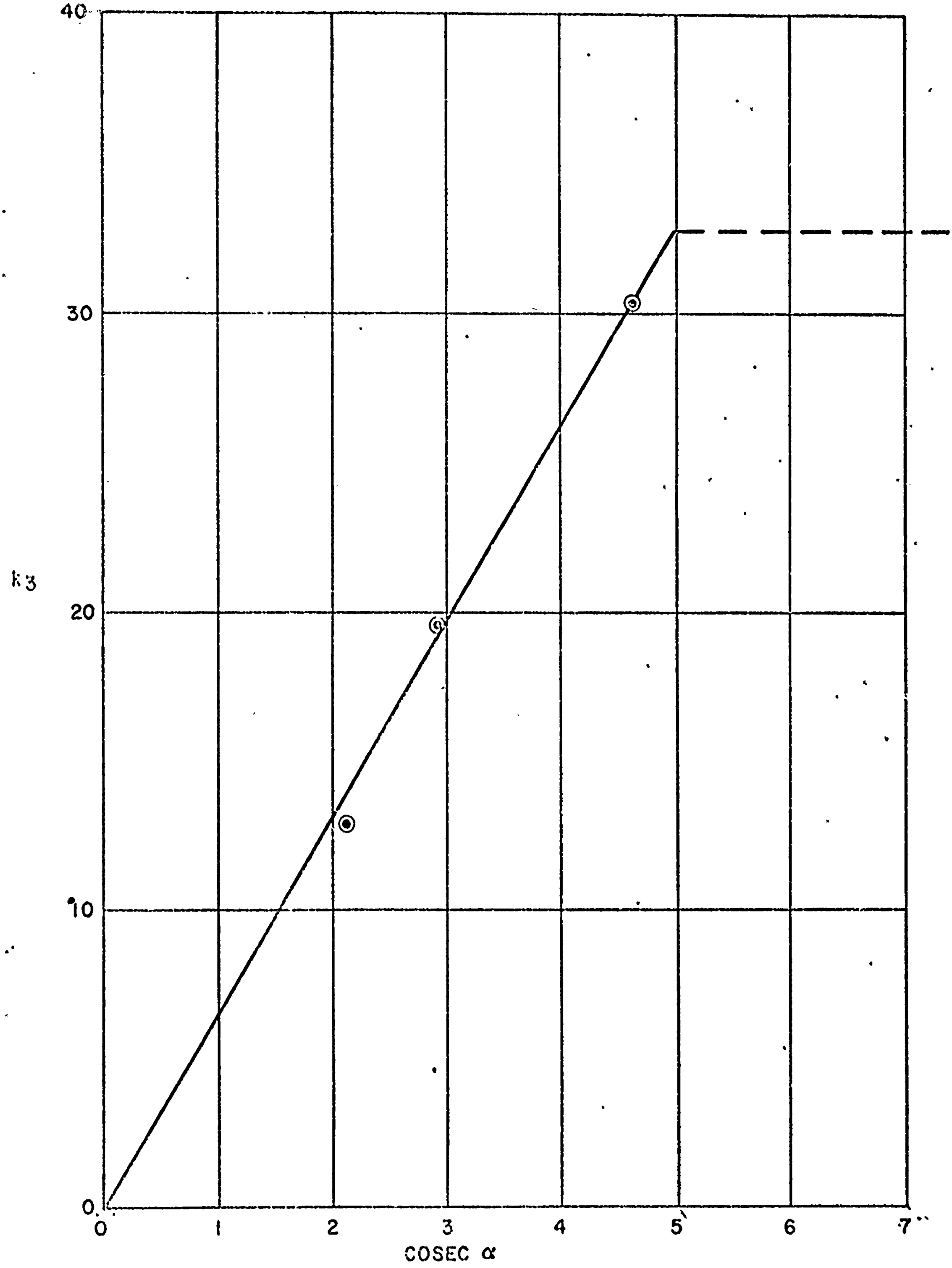

Figure 8. The Slope k_3 of the Lines in Figure 7 as a Function of cosec α When α Denotes the Inclination of the Tube.

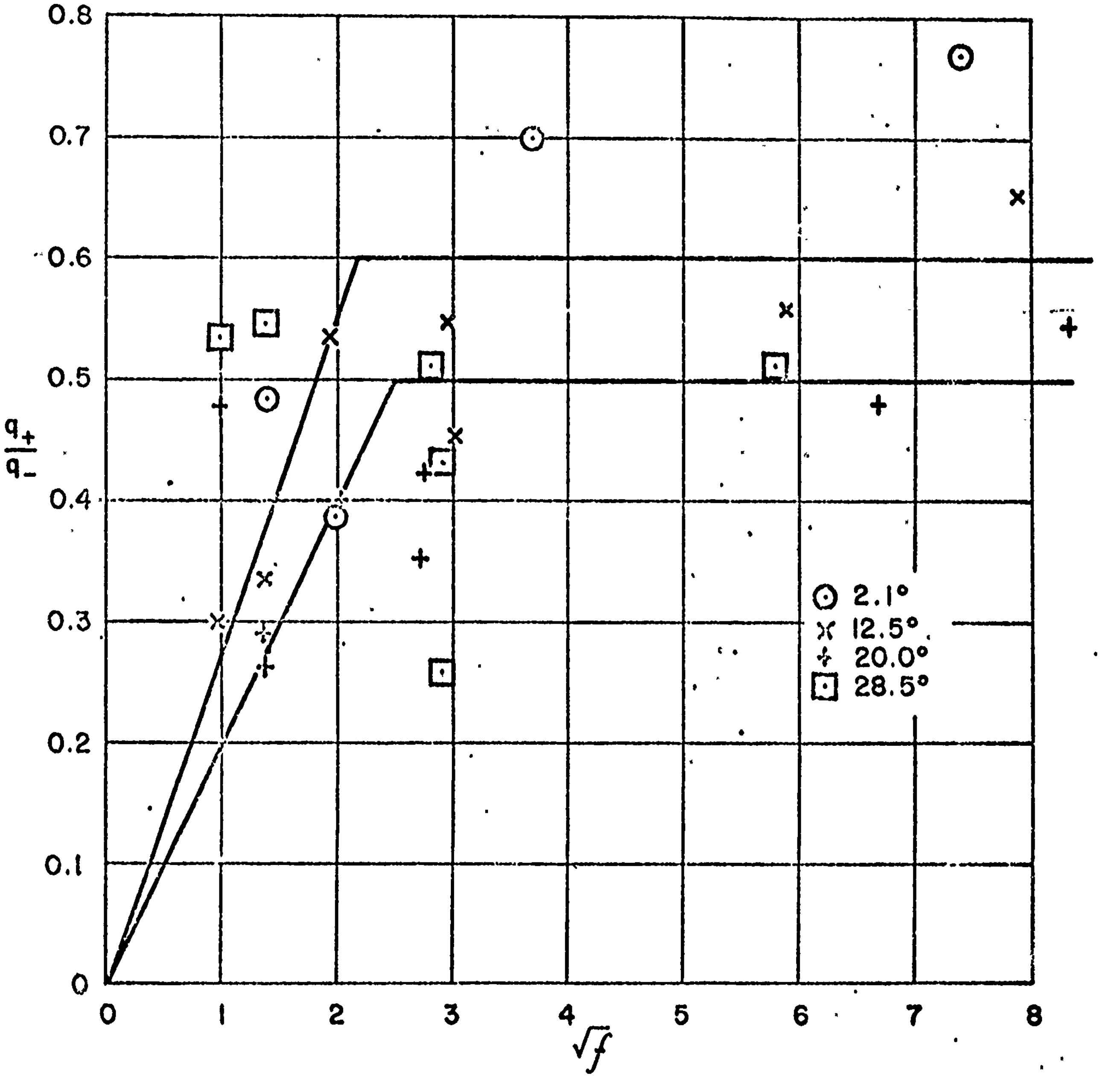

Figure 9 Ratio of Average Positive Charge q_+ to Average Negative Charge q_- on the Balls as a Function of $\sqrt{f}$ at Various Inclinations of the Tube

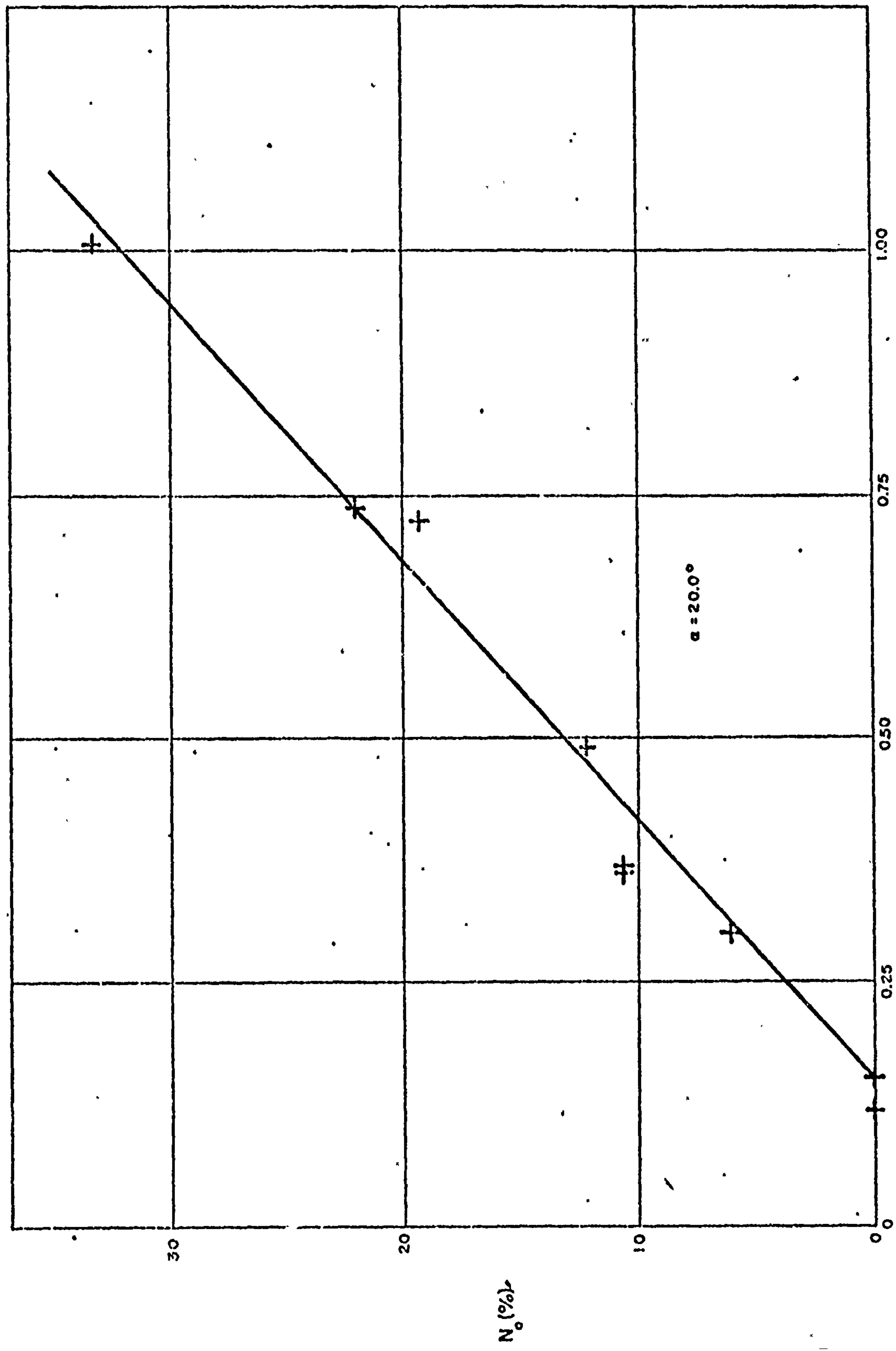

Figure 10. The Percentage of Neutral-Glass Balls N_o as a Function of $\frac{1}{\sqrt{f}}$

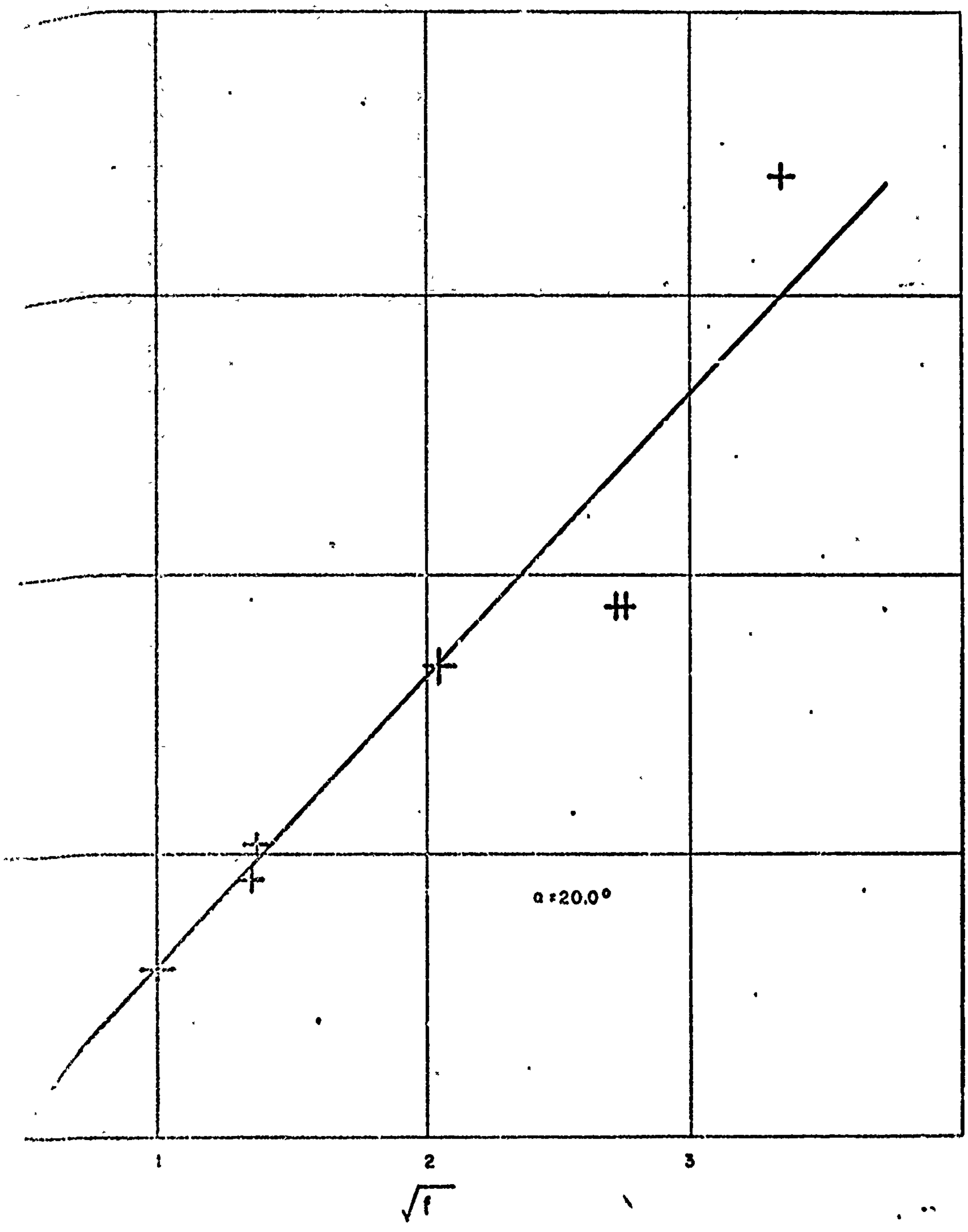

Figure 11. $\frac{1}{N_o}$ as a Function of $\sqrt{f}$.

The value N_+ of the percentage of positive balls follows a plot very similar to that of q. Figure 7 shows N_+ as a function of $\sqrt{f}$. The plot is linear at small values of f and reaches a saturation level of 50 - 60 percent that seems to be independent of α. The slopes k_3 of the straight lines in Figure 7 are plotted against cosec α in Figure 8. A straight line is obtained in the range $12.5 \leqq \alpha \leqq 28.5^\circ$. The values of $k_3 \sin\alpha$ are given in Table 1. The value of k_3 at $\alpha = 2.1^\circ$ is the same as that at $\alpha = 12.5^\circ$. Thus,

$$N_+ = k_3\sqrt{f} \qquad \text{for small values of } f \qquad (3)$$

$$k_3 = k_4 \operatorname{cosec}\alpha \qquad \text{for large values of } \alpha \qquad (4)$$

The time spent by each ball in the tube, assuming zero initial velocity, is

$$\tau = \sqrt{\frac{2L}{g\sin\alpha}} \qquad (5)$$

when L is the length of the tube and g is the acceleration of gravity. Accordingly,

$$k_1 = k_2\tau \qquad \text{for small values of } \tau \qquad (6)$$

$$k_3 = k_4\tau^2 \qquad \text{for small values of } \tau \qquad (7)$$

For "normal" balls, small values of τ are below 1 second.

The time t between successive balls is

$$t = \frac{1}{f} \qquad (8)$$

Combining these formulae we obtain

$$q = k_2\tau\frac{1}{\sqrt{t}} \qquad \text{for small values of } \tau \qquad (9)$$

$$q = k_2'\frac{1}{\sqrt{t}} \qquad \text{for large values of } \tau \qquad (10)$$

$$N_+ = k_4\tau^2\frac{1}{\sqrt{t}} \qquad \text{for small values of } \tau \text{ and } \frac{1}{t} \qquad (11)$$

$$N_+ = k_4'\tau^2 \qquad \text{for small values of } \tau \text{ and } t \qquad (12)$$

$$N_+ = k_4'\frac{1}{\sqrt{t}} \qquad \text{for large values of } \tau \text{ and } t \qquad (13)$$

$$N_+ = k_4'' \qquad \text{for large values of } \tau \text{ and } \frac{1}{t} \qquad (14)$$

Figure 9 shows a plot of the ratio of average positive charge q_+ to average negative charge q_- against square root of frequency f. As may be expected, this plot is similar to that for N_+ in Figure 7. There is a remarkable scatter of the data, but the data obtained at $\alpha = 12.5^\circ$ and $\alpha = 20.0^\circ$ seem to be adequately represented by the lines drawn in Figure 9.

The fraction N_o of uncharged balls, defined as those giving no deflection of the recorder, was determined. Figure 10 and Figure 11 show plots of N_o against $\sqrt{f}$ and of $\frac{1}{N_o}$ against $\sqrt{f}$, respectively. The definition of N_o being rather arbitrary, linked as it is to the response of the recorder, the significance of these plots should not be exaggerated. They show, however, that N_o comes to zero at a finite frequency and to unity at some small frequency close to zero.

4.2 SURFACE-TREATED BALLS

The effect of ultrasound upon oxygenated water is to produce H_2O_2. In aerated water, HNO_2 and HNO_3 are formed in addition to H_2O_2. The balls treated with ultrasound in water under O_2, N_2, and air were run like the "normal" balls, although less extensively. Table 2 shows the ratio between the average absolute charge of these balls and those of "normal" balls at $\alpha = 20^\circ$ and at f = 7 and f = 28 balls per minute. This ratio is based on the curve drawn in Figure 5 for $\alpha = 20.0^\circ$ and the average of three runs for the treated balls.

TABLE 2.

		f = 7	f = 28 balls per minute
"Normal" balls	q	6.75	13.50
Balls treated under O_2	q	6.30	9.96
	ratio	0.93	0.74
Balls treated under N_2	q	8.27	12.57
	ratio	1.22	0.94
Balls treated under air	q	4.23	5.21
	ratio	0.63	0.39

It follows from this comparison that treatment under O_2 or N_2 does not appreciably change the balls and that treatment under air reduces the average absolute charge of the balls. The effect of treatment under air is particularly conspicuous in the fraction N_+ of positive balls: in the first run, at $f = 7$ balls per minute, there was not one positive ball among a total of 217 balls.

It was noticed that the value of N_+ increased as the experiments were repeated. This change was not related to time of storage, but it was simply related to the number n of runs as shown in Figure 12. Thus,

$$N_+ = k_5 n^2 \tag{15}$$

This result shows that the formula (4) holds for a much longer time, $n\tau$, for these balls as compared to "normal" balls. Parallel to this increase in N_+ there was an increase in q_+, but this increase occurred at the expense of q_-, and there was no trend in the values of q.

Two attempts at reproducing the result (15) were made. Figure 13 shows the two plots of N_+ against n for these runs. Although the result (15) was not reproduced, these latter results show that N_+ increases with n up to close to 90 percent. It should be pointed out that the same tube was used in all these experiments and that nitrite and nitrate were probably rubbed off the balls onto the tube wall. This may account for the differences between the three runs.

The data in Table 2 suggest that the balls exposed to ultrasound in aerated water reach a limiting value of the average absolute charge that does not increase with a further increase in frequency. In order to check this point, a new set of balls thus treated were prepared and run at 1, 4, 7, and 28 balls per minute. The result is shown in Figure 14.

4.3 EFFECT OF THE ATMOSPHERE

As already pointed out, the apparatus used in these studies does not permit the use of controlled atmospheres in the glass tube. However, a few qualitative tests were made in which gases were blown through the tube.

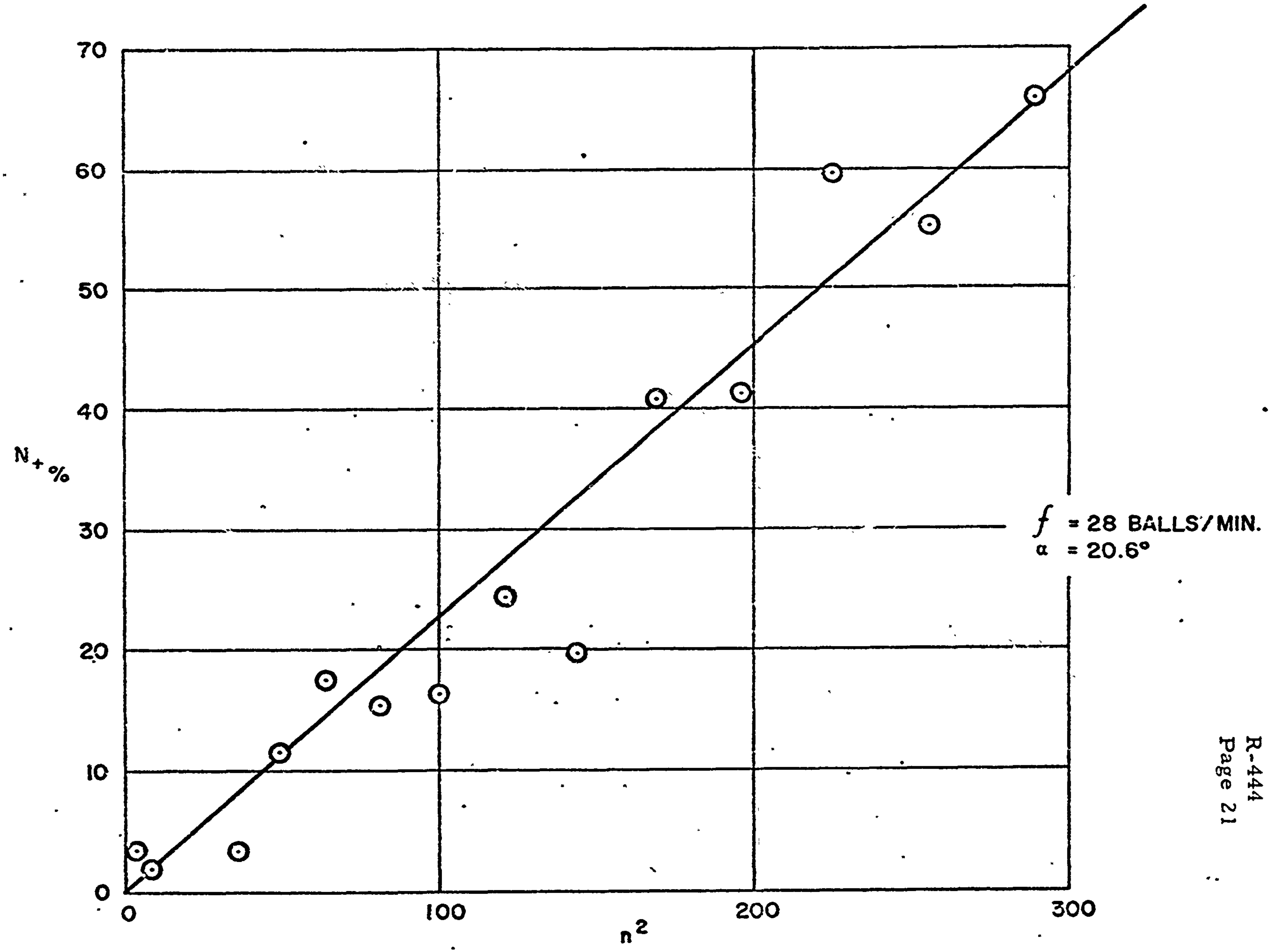

Figure 12. Fraction N_{+} of Positive Balls as a Function of the Square of the Number n of Successive Runs After Treatment of Balls with Ultrasound in Aerated Water.

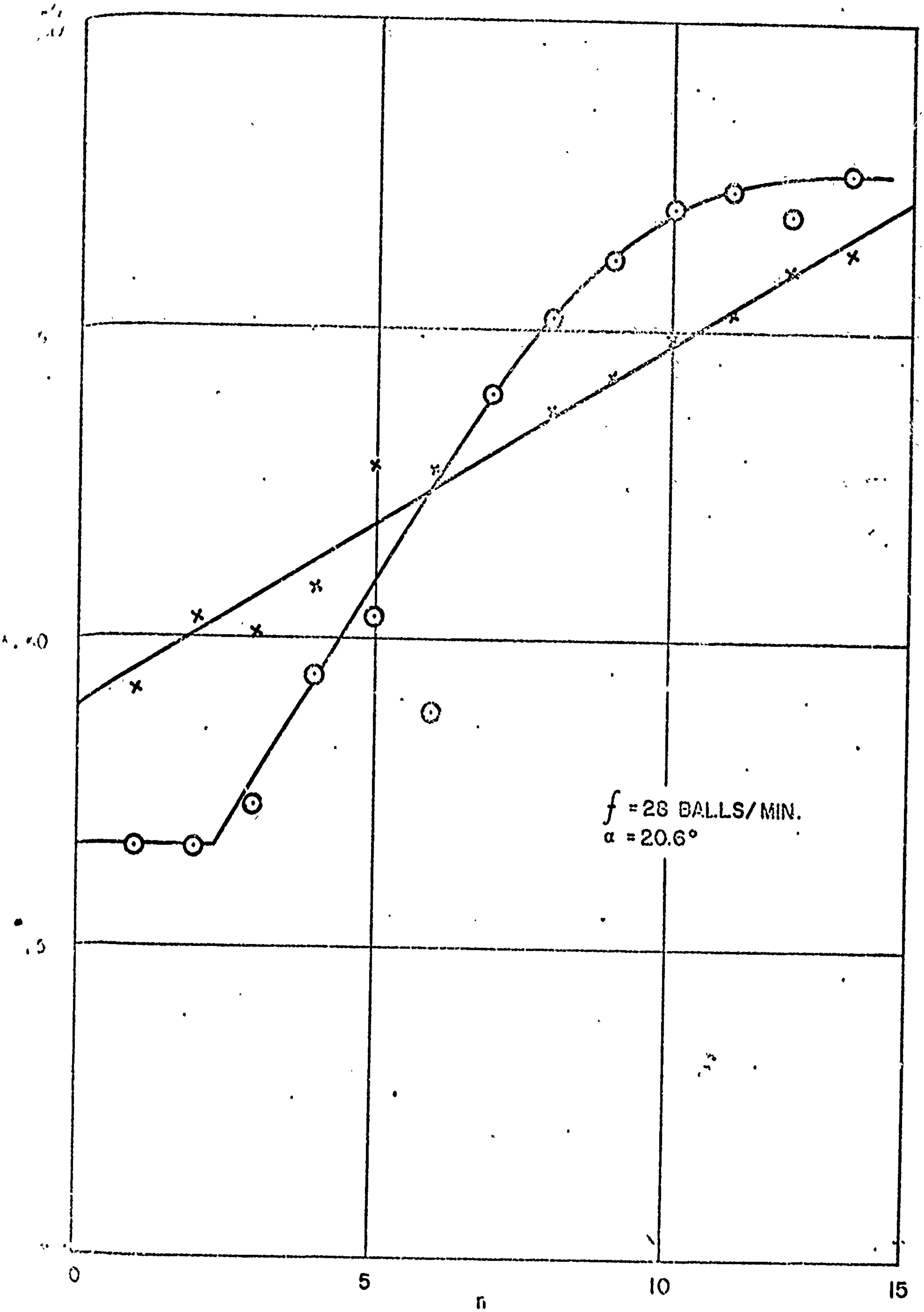

Figure 13. Fraction N_+ of Positive Balls as a Function of the Number n of Successive Runs After Treatment of Balls with Ultrasound in

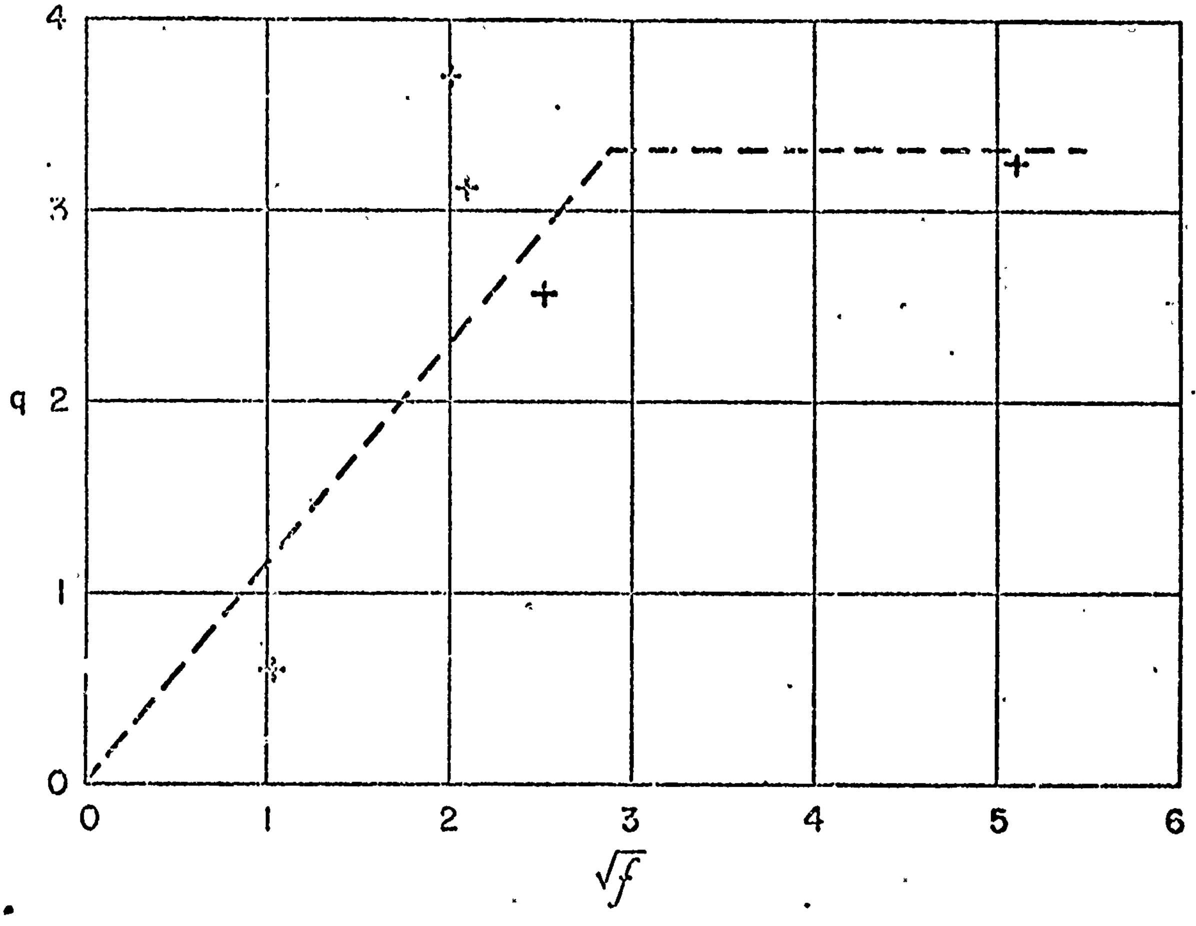

Figure 14. Average Absolute Charge q as a Function of $\sqrt{f}$ For Balls Treated with Ultrasound in Aerated Water.

Breathing down the tube caused condensation of water on the tube wall. In this state no charge was obtained. Slight breathing that did not cause condensation reduced the charge; the positive charge was reduced much more than was the negative charge.

Flushing the tube with N_2 slightly increased the average charge but had little effect on the ratio of positive to negative balls.

Flushing the tube with O_2 increased the average charge by a factor of 2.5 and completely suppressed the positive charges.

4.4 QUALITATIVE OBSERVATIONS

Within the experimental accuracy there was no noticeable effect of variations in temperature (60 - 80° F) and relative humidity (50 - 30 percent) upon the quantities observed. The average absolute charge seemed to decrease somewhat with increasing humidity.

Owing to variations in size and roundness of the glass balls, it occurred occasionally that two balls were delivered together or with a short interval into the glass tube. Numerous such pairs were recorded. There was no relation between such balls as to sign and magnitude of charge.

It was thought that the charges would be removed from the balls partly in the Faraday cage and finally in the feeding device. This turned out to be wrong. The balls entering the glass tube were charged. In order to check this further, the balls were conducted through a ground-connected copper tube between the glass tube and the Faraday cage. This had no noticeable effect on the voltage of the Faraday cage, and it made no difference whether the balls rolled on the wall of the ground-connected copper tube or dropped through it without touching the wall. Although, thus, passage through the ground-connected copper tube did not remove the charge from the balls, it was observed that the first ball of each run, particularly after a long delay since the preceding run, gave no charge to the Faraday cage, and that a stationary state of charge was built up gradually by the first few balls.

5. THEORY

As was pointed out in Section 1, H and OH are instrumental in electron transfer processes in general and in the electrification by friction in particular. The source of H and OH is H_2O in the atmosphere or in the solid bodies. In these experiments, H_2O was abundant to the extent that its reaction, particularly the heterogeneous formation of and OH, may be assumed to be rapid. Rate-determining in the formation of charge and in its distribution upon balls and tube should then be subsequent reactions of H and OH.

The identification of the reaction mechanism requires quantitative study of the effects of the pertinent species, i.e., measurements in controlled atmospheres. Such study is planned as a continuation of this investigation. Meanwhile, information may be derived from the results reported in Section 4.

In the interpretation of the data it should be borne in mind that the data do not pertain immediately to generation of charge but to distribution of charge. In terms of electron transfer, the data pertain to the difference between the rates of electron transfer in the two directions ball-tube and tube ball. The system ball-tube constitutes a rectifier for the flow of charge whatever the source of charge may be. On the other hand, the amount of charge on the ball depends not only upon the relative distribution of charge but also upon the total amount of charge to be distributed.

The fact that N_+ increases with $\mathcal{T}$ shows that the charge on the ball changes its sign during the passage of the ball through the tube and with a tendency to becoming more positive up to a certain limiting value of $\mathcal{T}$, above which positively and negatively charged balls are approximately equally abundant. It seems to follow that ball and tube rub off on each other until their surfaces are equal, whereupon the probability of charge of one sign on either of the two is the same. This conclusion is borne out by the observation that fresh balls and tubes behave differently from balls and tubes worn in together.

The fact that N_+ increases with f shows then that the result of this equalization decays with time. However, above a certain limiting value of f, N_+ is independent of f and is approximately 50 percent. At this state, the decay no more affects N_+ but it continues to affect q.

The value of q increases with τ up to a certain limiting value, which is the same as that for N_+. But q continues to increase with f, far beyond the limiting value for N_+.

These observations suggest that the total charge increases with f, at least above a certain value of f, and that τ essentially affects the distribution of charge. If this conclusion is correct, the charge generation decays according to formula (1). This means that each ball passing through the tube creates a state in the tube that is instrumental in the generation of charge.

Clearly, the decay of the charge-generating state proportionally to $\frac{1}{\sqrt{t}}$ may be accounted for in several ways. The evidence indicates surface phenomena rather than phenomena in the gas volume of the glass tube. Such evidence is the profound effect of surface treatment and the negligible effect of blowing N_2 through the tube.

The pertinent heterogeneous reactions have been treated in preceding papers[11-13]. The decomposition of H_2O on an oxide (glass) surface is enormously accelerated by traces of a hydrogen-replacing metal. Such metal is present in the glass, e.g., Na. At a stationary state, when reduction and oxidation are at a balance, the amount of such metal on the surface is constant, and reactions occur preferentially on and at exposed free metal[13]. On such metal, the equilibrium

$$H_2O_{ads} \rightleftharpoons H_{metal} + OH_{ads} \qquad (16)$$

is rapidly established. Denoting coverages by brackets and concentration in solution in the metal by braces, this equilibrium gives

$$\{H\} [OH] = K'' [H_2O] \qquad (17)$$

In the case at hand, at high H_2O vapor pressures, $[H_2O]$ is close to unity and 11-13)

$$[OH] = \frac{K''}{[H]} \tag{18}$$

The fraction of free absorption sites is 11-13)

$$(1 - \theta) = \frac{K}{(H_2O)} \tag{19}$$

when (H_2O) denotes the water vapor pressure and K is the equilibrium constant in

$$(H_2O)(1 - \theta) = K[H_2O] \tag{20}$$

Absorption of H occurs by the reaction 11-13)

$$H_2 + OH_{ads} \longrightarrow H_{metal} + H_2O_{ads} \tag{21}$$

and at the rate

$$\frac{d\{H\}}{dt} = k_6(H_2)\,[OH]\,(1 - \theta) \tag{22}$$

Integration gives

$$\{H\} = \sqrt{k_6KK''}\,\frac{(H_2)^{1/2}}{(H_2O)^{1/2}}\,\sqrt{t} \tag{23}$$

In the case at hand, the value of (H_2) just above the surface is a constant that is determined by the rate of escape of H_2 from the surface into a vacuum, and the value of (H_2O) is also a constant. Accordingly, from equations (18) and (23),

$$[OH] = \frac{k_7}{\sqrt{t}} \tag{24}$$

It should be pointed out that, at a stationary state, the rate of absorption of H is equal to the rate of desorption of H_2, although these processes occur at different spots on the surface, and it is also equal to the rate of oxidation of metal and reduction of oxide. Absorption of H occurs at spots of reduction, desorption of H_2 occurs at spots of oxidation. These phenomena have been discussed in detail elsewhere 13).

Comparing the formulae (1) and (24) we find that q is proportional to $[OH]$. Thus the case of heterogeneous reaction of OH is compatible with the empirical formula (1).

Let us consider two surfaces in contact, both of which consist of oxide with islands of free metal. For simplicity, the oxide will first be disregarded as a chemical species and considered as an electrical insulator only. The free metal is partly covered with H_2O, partly with OH, and is partly bare. The reason why there are undecomposed H_2O molecules is that they have no adjacent free adsorption site. If now an H_2O site on one surface comes in contact with a free site on the other surface, this H_2O molecule decomposes into H and OH. If the free site is adjacent to an OH site and receives an H atom, the two combine and the result is that an OH on one surface and an H_2O on the other surface have changed places. There is no charge transfer in this process. If, however, the free site that receives the H atom is not adjacent to an OH site, the H atom goes into the metal and charge transfer occurs so that the receiver of H becomes positive and the other, the receiver of OH, becomes negative. Since $\{H\}$ increases for the receiver of H, its number of OH sites decreases and its ability to receive H under charge transfer increases. By the same token, the receiver of OH loses ability to receive H under charge transfer. Thus, if an island starts to charge positively, it will continue to charge positively. The process continues until $[H_2O]$, $[OH]$, and $\{H\}$ are equal for both metals. From there on there is no further net transfer of charge. The charge is thus proportional to the total time of contact τ, up to a certain limiting value, as found empirically.

If now one surface, the ball, is at equilibrium with the atmosphere while the other surface, the tube, has an excess of OH as compared to the equilibrium, the ball island will be positively and the tube island negatively charged, the amount of charge being proportional to the excess of OH above that at equilibrium. Since, according to formula (24), the excess of OH is proportional to $\frac{1}{\sqrt{t}}$, the amount of positive charge on the ball island is proportional to $\frac{1}{\sqrt{t}}$ as found empirically.

Let us now consider the oxide at the edge of the metal island. If the ball island is at equilibrium with the atmosphere while the tube island is not, the OH density at the edge of the ball island is still higher than the OH density on the tube island. There will therefore be an exchange of OH and H_2O, as previously described, at the edges. This process will continue until the islands become, on the average, equal on both surfaces.

Clearly, the more total free metal there is on one surface, the smaller is the edge effect and the smaller the over-all density of OH at equilibrium. Hence, the more total free metal, the more positive charge. Therefore, soda glass should be positive with respect to Pyrex, and a ball of a glass intermediate between soda glass and Pyrex should be negative with respect to soda glass and positive with respect to Pyrex. This is in agreement with observation. On the other hand, with prolonged rubbing, the metal-rich glass will reduce whatever metal there is in the metal-poor glass and the difference will be correspondingly reduced. This is also in agreement with observation.

The exchange just referred to, by which the metal-rich surface reduces out more metal on the metal-poor surface, does not occur perfectly uniformly. Some balls "rub off" more, other balls less. A state will therefore be established in which the balls and the length of the tube are covered, on the average, by equal amounts of free metal. At this state, irrespectively of the bulk analyses, there are equal numbers of positive and negative balls above certain values of τ and f.

The mechanism outlined above is corroborated by the observed effects of N_2 and O_2 blown through the tube. N_2, that has little effect on OH, has little effect upon the charge. O_2, however, that reacts with H to form OH according to the formula

$$O_2 + 2H_{metal} \longrightarrow H_2O_{2\ ads} \longrightarrow 2\ OH_{ads} \qquad (25)$$

has a drastic effect upon the balls, which are at equilibrium with the ambient atmosphere and contain much H. It makes all the balls negative by increasing their $[OH]$. It also increases the average charge that is proportional to $[OH]$.

The oxidation-reduction mechanism and the charge transfer mechanism according to formula (1) are, fundamentally, those of electrochemical potential. The electrochemical aspect has been emphasized by Wolf 14) who considered transfer of metallic ions to a film of water on the insulator as the essence of electrification in friction. In the experimental pursuit of this view, Wolf showed that the sign of the charge may be reversed by the application of an electric field of suitable magnitude and direction. The electrochemical aspect is borne out by a comparison between the potentials of metals rubbed against SiO_2 and their standard electrode potentials. This comparison is shown in Figure 15 on the data of Shaw and Leavey 15) and the electrode potentials given by Cooke 16).

6. CONCLUSION

The experimental technique used in this investigation permits the quantitive study of electrification in friction. The choice of nearly equal materials in the friction couple eliminates unessentials and directs the attention to the basic mechanism of electrification.

The data show that the essence of this mechanism is the disturbance of the equilibrium between the surface and the atmosphere as a result of friction and the subsequent equalization of the disturbed surfaces to each other and with the atmosphere.

Although the identification of the details of the electrification mechanism requires the study of the effect of the atmosphere, the main features of the mechanism can be derived from the results obtained in the ambient atmosphere.

The results are compatible with the general mechanism for electron transfer as outlined in Section 1. The role of water requires surface reactions of the water with the glass, the mechanisms of which were worked out in detail in a previous investigation 13). It consists in oxidation-reduction processes involving the silicate of the glass and free metal reduced out from the silicate.

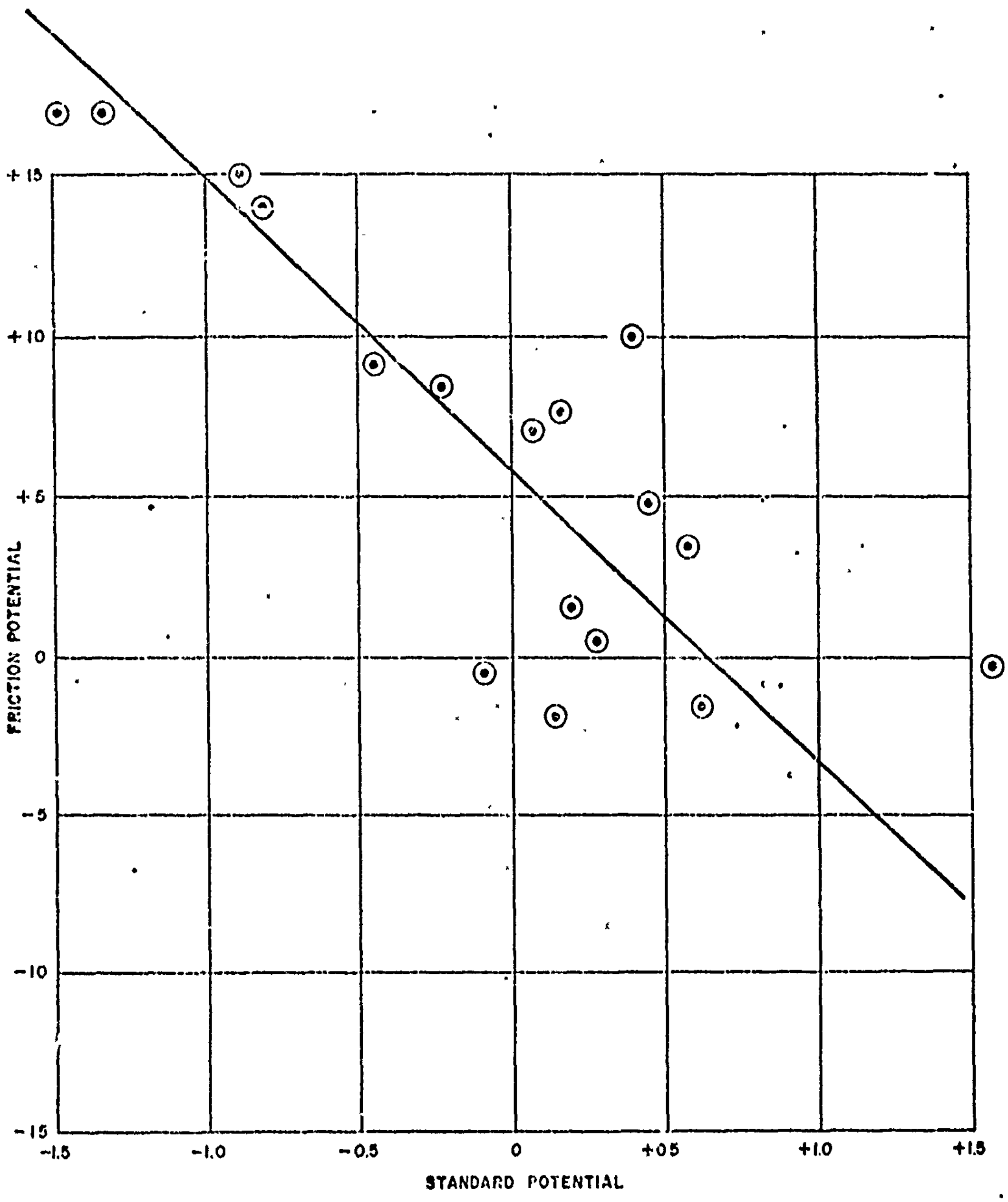

Figure 15. Friction Potentials of Various Metals in Friction Against SiO_2 Plotted Against their Standard Electrode Potentials.

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