the Royal Society, 186 A, p. 343. These curves include six types besides the normal curve, but the book makes no reference to the five additional types of curves recently published by Pearson.[1] The book presents a treatment of the correlation of two systems of variates. The treatment is, in general, clear, and should serve a useful purpose in making better known to persons who are applying these methods to data the nature of some of the limitations that underlie the interpretations of correlation coefficients. However, the reviewer has one criticism to offer. On p. 155, using $r$ for the correlation coefficient, we are told that "it seems doubtful whether any serious meaning can be attached to values of $r$ which are less than .5." It seems to the reviewer that this statement should be modified. To be sure, the statement would hold if the correlation coefficient $r$ were calculated from such a small number of observations that the probable error of $r$ is not particularly small compared to $r$. But when the conditions under which the formula for probable error of $r$ is derived are well satisfied, $r$ may be much smaller than 0.5 and have decided significance if derived from large enough number of observations to make its probable error small in comparison to the value of $r$.

A useful chapter is devoted to harmonic analysis from the standpoint of least squares, including an interesting section on a practical method of investigating periodicities. The last chapter deals with the periodogram, including a treatment of hidden periodicities.

H. L. Rietz

University of Illinois

## SPECIAL ARTICLES

### THE PRODUCTION OF GASEOUS IONS AND THEIR RECOMBINATION

Gaseous ionization has played a large part in recent advances in both physics and chemistry. In the ordinary college- and high-school courses given in these subjects little, if any, attempt is made, however, to demonstrate methods of producing gaseous ions or of measuring their recombination or diffusion constants. Practically no laboratory work along these lines by elementary students is attempted. This may be explained in part by the fact that most investigators in this field of research have made use of the electrometer, an instrument well adapted for demonstration purposes but inappropriate for use by the inexperienced student. An electroscope of very simple design has, however, proved entirely satisfactory in place of the more cumbersome and possibly less sensitive electrometer.

Some elementary experiments are suggested in the first part of this paper using apparatus involving little or no expense and which may be assembled by any high-school student. This is followed by a description of some results obtained in verification of the law governing the recombination of the ions of a gas.

#### PART I

The type of electroscope used is shown in Fig. 1.

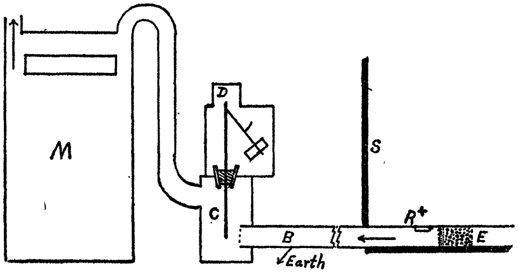

Fig. 1.

A brass rod passes through a sulphur plug into the hollow cylindrical chamber ($C$) 12 cm. high and of 4 cm. radius. On this rod is mounted a flat brass strip which supports the gold leaf. The top of this mounting projects through a large opening in the square metal box surrounding the gold leaf to permit the electroscope to be charged by removing the metal cap ($D$). ($B$) is a brass tube approximately 2 meters long the radius of which will depend upon the laboratory facilities for providing a suitable current of gas. If air ionization is to be studied and compressed air is not available, a suction pump attached to a water faucet will provide a convenient velocity for carrying ionized air through ($B$) if its radius is of approximately 3 cm. diameter.

---

[1] *Phil. Trans.*, 216 A, p. 429.

The velocity of the ions and consequently the time taken for their passage over a given distance may be obtained by measuring the volume of air passing in a given time. A common gas meter (*M*) provided with a dial one turn of which registered one half of a cubic foot was used in these experiments. The air passing through the tube may be dried by calcium chloride and ions prevented from entering with the air stream by a plug of cotton wool placed at (*E*). Lead screens (*S*) should be erected to shield the electroscope from direct radiation. Provided radium salt be used as ionizing agent at a short distance from the electroscope, these screens will need to be several centimeters thick.

The gas passing through the tube may be ionized by X-rays or $\gamma$-rays shot through a slit (*R*) cut in the tube and covered by a thin mica sheet, or the ionizing source may be placed inside the tube. A 2 or 3 mm. spark between the secondaries of an induction coil sealed into the tube provides a convenient source of ionization for demonstration purposes. X-rays also produce powerful ionization effects. A 2-inch X-ray bulb run at dull luminescence by a coil capable of producing a 4 cm. spark will provide sufficient ionization for the experiments described below.

A Nernst lamp is more suitable for projecting the gold leaf on a screen than the ordinary lantern. For laboratory work a low powered microscope with a divided scale in the eye piece is used for measuring the rate of fall of the gold leaf.

An electroscope of the type shown in Fig. 1 may be made of comparatively small capacity. If the leaf be charged to a relatively high potential, it becomes an instrument of high sensibility. Owing to the extremely small mass of the gold leaf it will rapidly alter its rate of deflection as the number of ions swept into the chamber changes.

Place the X-ray bulb directly over the electroscope and charge the gold leaf, by means of an ebonite rod, till it shows large divergence. Run the bulb for an instant and the gold leaf at once drops a distance proportional to the ionization produced in the electroscope by direct radiation. If the charging cap is not replaced before starting the bulb, the sudden drop takes place as before, but the leaf instead of stopping its motion as suddenly as it began gradually slows up with time. This effect is produced by the ions in the air surrounding the electroscope rapidly diffusing into it, the number diminishing as recombination takes place. Some idea of the rapidity with which the leaf comes to rest may be obtained from Table I. The numbers represent readings on the scale between the intervals stated in the first column. The readings with 3 second intervals were observed and recorded without assistance. Shorter intervals required assistance in making the record.

TABLE I

| Interval | Exp. 1 | Exp. 2 | Exp. 3 | Exp. 4 | Exp. 5 | Exp. 6 |
|---|---|---|---|---|---|---|
| 3 secs. | 9 | 17 | 7 | 28 | 34 | 55 |
| | 21 | 28 | 15 | 43 | 41 | 74 |
| | 27 | 33 | 19 | 49 | 45 | 78 |
| | 30 | 36 | 22 | 53 | 47 | 80 |
| | 31.5 | 38.2 | 24 | 55.5 | 48.5 | 81.2 |
| | 32.5 | 39.5 | 24.8 | 57 | 49.2 | 81.8 |
| 2 secs. | 59 | 48 | 74 | 65 | 84 | 29 |
| | 65 | 54 | 80 | 71 | 88 | 33 |
| | 70 | 57 | 84 | 74 | 91 | 35.5 |
| | 73 | 59.5 | 87 | 76 | 93 | 36.6 |
| | 74.8 | 60.5 | 88.5 | | 93.8 | |
| | | | | | 94.5 | |
| 1.67 secs. | 71 | 75 | 77 | 68 | 64 | 32.5 |
| | 74.5 | 79 | 79.5 | 71 | 68 | 36.5 |
| | 76.4 | 82 | 80 | 72.3 | 70 | 39 |
| | 77.4 | 83 | 80.8 | 73.5 | 71.6 | 40 |
| | | 84.2 | 81.2 | | 73 | |
| | | 84.6 | | | 73.6 | |

Place the X-ray bulb over the slit as indicated in Fig. 1 and start the suction pump. When the radiation passes through the slit large quantities of positive and negative ions are produced in the air stream directly beneath. If the bulb is but a short distance from the electroscope and the air velocity is high, a large proportion of the ions originally produced will be swept into the chamber causing a rapid rate of fall of the gold leaf. The remainder have either recombined or diffused to the side of the tube. Since the negative ions diffuse more rapidly than the positive, the tube should be earth connected. When the bulb or spark gap is 2 or 3 meters from the electroscope and the air velocity is diminished, a considerable time will elapse before any of the ions can reach the electroscope and these will be but a small percentage of the number originally present.

As the first ions arriving are swept into the chamber of the electroscope the leaf begins to move and its rate of fall increases and finally reaches a constant value which is maintained until a short time after the X-rays (or spark) is stopped, following which the rate of leak slowly reduces to zero. The apparent slowness of the leaf in starting and stopping is largely due to the effect of friction between the air and the inner surface of the tube. This appreciably diminishes the velocity of the air in that region, so that on starting, ions passing through the central portion of the tube arrive first. After the rays are stopped, ions near the surface trail along behind, gradually decreasing in number as recombination and diffusion proceed. The effect will of course vary with the length, diameter and material of the tube and the velocity of the air. It will later be shown that this irregular distribution of ions in the tube may affect the value obtained for the recombination constant. For high velocity and a short length of tube the leaf starts at once with a uniform rate of deflection and stops abruptly. Using a spark gap 2 meters from the electroscope and a slow air current, a relatively large rate of leak was observed after 35 seconds had elapsed between the stoppage of the spark and the arrival of the first ions in the chamber.

The rapidity with which gaseous ions diffuse may be well illustrated by inserting a compact bundle of tiny, thin-walled metal tubes inside the tube near the slit. These should be soldered together and make good contact with the inner surface of the tube. Diffusion takes place so rapidly, as the ions pass through the tubes, that with the same air velocity and ionizing source, the number of ions reaching the electroscope is enormously diminished.

The effect of water vapor or dust particles in increasing the ionization, where otherwise the conditions of experiment remain unchanged, is easily demonstrated.

### PART II

### *Experimental Proof of the Law of Recombination*

Rutherford has shown that the rate of recombination, at a given instant, of the ions produced in gases exposed to X-rays[1] and the radiation from uranium[2] is proportional to the square of the number present at that instant, from which it follows that

$$\frac{1}{n}-\frac{1}{N}=at,$$

where $N$ and $n$ are the number of ions present in the gas at the beginning and end of time $t$, respectively. This law has also been verified for gases exposed to X-rays by McClung[3] also by McClelland[4] using arcs and flames as the ionizing agents.

The method most generally employed when large quantities of the gas are available has been to pass the ionized gas through an earthed metal tube with constant velocity and measure the saturation currents at different points along the tube by means of an electrometer. A gas meter was used to measure the velocity through the tube as already intimated.

The deflection of the electrometer indicates the number of ions in a certain portion of the tube at a given instant. The fall of the gold leaf of an electroscope is, however, an integrating process like that of the gas meter and continues over a considerable time for each reading.

If the ionizing agent or the velocity of the ions themselves should undergo slight changes, the rate of fall of the gold leaf would give a good indication of the average number of ions passing at a given time. The sensibility of the electroscope will also remain fairly constant over long intervals and is readily tested.

In the course of some work involving the use of X-rays and $\gamma$-rays from radium salt, it

---

[1] Rutherford, *Phil. Mag.*, V., 44, p. 422, 1897.

[2] Rutherford, *Phil. Mag.*, V., 47, p. 142, 1899.

[3] McClung, *Phil. Mag.*, VI., 3, p. 283, 1902.

[4] McClelland, *Phil. Mag.*, V., 46, p. 29, 1898.

was necessary to measure their relative ionizing effects at a given point in air. This was accomplished by sucking the ionized air from the vicinity of the given point through a metal tube into the chamber of an electroscope placed at some distance, as shown in Fig. 1. By noting the rate of deflection of the gold leaf for different air velocities curves corresponding to decay curves were plotted, using ionization in divisions per minute as ordinates and the times of passage of the ions through the tube as abscissæ. By continuing these curves back to zero time an approximation was obtained of the relative ionization originally present. A more exact estimate was made by obtaining the recombination constants for the two ionizing agents and, assuming the square law, calculating the original ionization when the ionization after a given time was known. This work suggested a further study of the recombination constants by this method, using various ionizers, and an examination of the recombination constants for ions produced by "hard" X-rays or the more penetrating $\gamma$-rays as compared with these values for the softer and less penetrating radiations.

Before using the electroscope as an indicator of the number of ions present at any instant, it was necessary to determine the deflection to which the gold leaf must be charged in order to obtain saturation conditions for the maximum velocity utilized. This was found by passing the ionized gas through the chamber of the electroscope to be used, then through the chamber of a second electroscope of high sensibility in close proximity to the one to be tested. The gold leaf of the latter was then charged to a potential sufficient to give no leak in the auxiliary electroscope. For lower potentials ions escaped into the second electroscope and the rate of leak of the first did not give a true indication of the number of ions passing into it. When the potential to which the leaf is charged is considerably lower than that necessary for saturation the decay curves obtained may show a maximum point, since there may be a critical velocity at which a maximum number of ions will give up their charges to the electroscope. At such a velocity the gain in the number entering the chamber will be counterbalanced by the number escaping without giving up their charges.

The order of experiment was then as follows: Determine the saturation potential necessary for a given position of an ionizing agent at the maximum velocity to be used. Obtain the natural leak of the electroscope when the ionizing agent was present, but with no current passing through the tube. Obtain rates of deflection of the leaf in divisions per minute for each of as large a number of different velocities as time and the capacity of the suction pump would permit. The leaf was charged to a given deflection and allowed to leak over the same number of divisions for each reading. The mean of several observations was taken at each velocity. Successive times for the flow of .5 cubic foot of gas through the meter at a given velocity were also recorded. These values were then plotted using ionization in divisions per minute as ordinates and cubic feet per minute as abscissæ. From the smooth curve thus obtained a number of points were chosen and the time of decay of the ionization to these given amounts calculated from the rates of flow. Two of the ionization values were then selected as representing $N$ and $n$ in the formula

$$\frac{1}{n}-\frac{1}{N}=\alpha t,$$

where $t$ was the difference between the calculated times of decay for the values chosen. Thus assuming the recombination law, $\alpha$ the recombination constant was calculated in arbitrary units. Using this value for $\alpha$, a number of values for $n$ were computed and compared with the experimental values. The ionizing agent was then placed at different distances from the electroscope and similar decay curves plotted as a series of checks and with the purpose of obtaining a better idea of the part played by diffusion. This was repeated for brass tubes of different diameters, using X-rays, $\gamma$-rays, electric sparks and black oxide of uranium as exciting agents. Air, carbon dioxide and oxygen were used as sources of ions. Decay curves were also obtained, using the arrangement shown in Fig. 2.

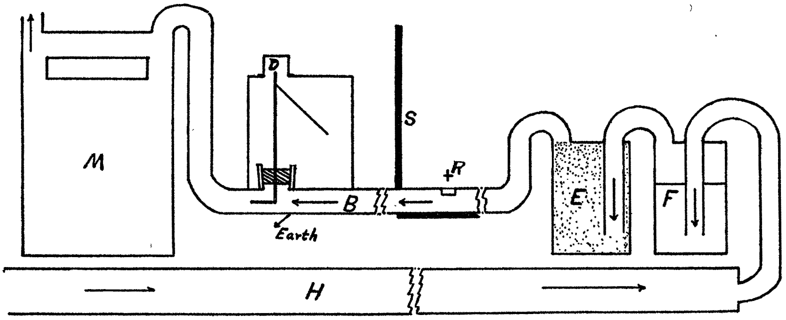

FIG. 2.

Air, oxygen or carbon dioxide under pressure was passed into a large metal cylinder (*H*) approximately 2 meters long, thence through two Wolff bottles (*F*) and (*E*) containing sulphuric acid and cotton wool, respectively, into the tube (*B*). The acid was used as a drying agent and the cotton wool to remove the ions produced by bubbling. This experimental arrangement permitted large velocities through tube (*B*).

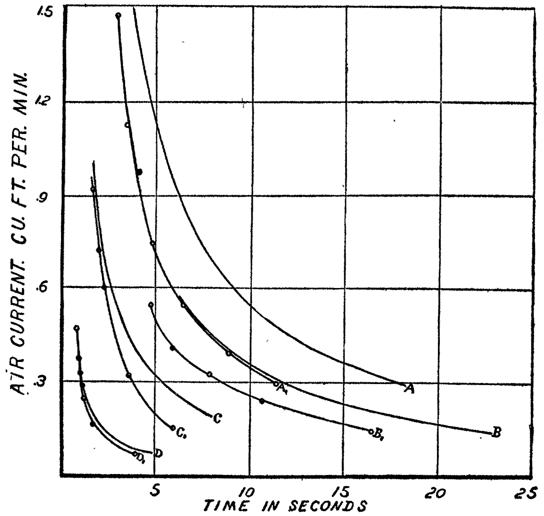

FIG. 3.

The natural leak of the electroscopes used throughout this work varied between .18 and .22 div. per min. with no ionizing agent present. With velocities of 2 cu. ft. per min. through the tube the leak of the electroscope due to ions escaping through (*E*) was less than .04 div. per min.

In some preliminary work it was found that, at a given velocity, ions passed through the tube in a shorter time than the time calculated from the rates of flow would indicate. Spark gaps were sealed into the tube at different distances from the electroscope and times elapsing between the starting of the spark and the beginning of the motion of the gold leaf were measured by a stop watch. For short

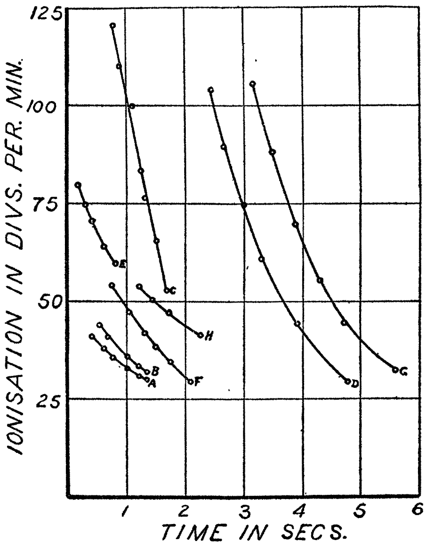

FIG. 4.

distances, the difference between observed and calculated times was negligible; for greater distances at slow velocities, the calculated times were considerably greater. In Fig. 3 curves are given, using rates of flow in cu. ft. per min. as ordinates and time in secs. as abscissæ.

TABLE II

| Curve | Ionizing Agent | Source of Ions | Dist. of Ionizing Agent from Elect. | Diam. of Tube | Drying Agent |
|---|---|---|---|---|---|
| *A*..... | .114 mg. rad. salt inside tube | Air under pressure | 16.8 cm. | 2.95 cm. | $H_2SO_4$ |
| *B*...... | .114 mg. rad. salt inside tube | Air suction pump | 16.8 cm. | 2.95 cm. | $CaCl_2$ |
| *C*...... | .300 mg. rad. salt above slit | Air suction pump | 27.7 cm. | 2.95 cm. | $CaCl_2$ |
| *D*..... | .300 mg. rad. salt above slit | Air suction pump | 93.1 cm. | 2.95 cm. | $CaCl_2$ |
| *E*..... | .114 mg. rad. salt inside tube | $CO_2$ under pressure | 16.8 cm. | 2.95 cm. | $H_2SO_4$ |
| *F*...... | .113 mg. rad. salt 1 cm. above slit | Oxygen | 29.0 cm. | 2.95 cm. | $H_2SO_4$ |
| *G*...... | *X*-rays | Air suction pump | 125.3 cm. | 2.95 cm. | $CaCl_2$ |
| *H*..... | Uran. cylinder | Air under pressure | 40.5 cm. | 5.2 cm. | $H_2SO_4$ |

Curves $A$ and $A_1$ are plotted, using the calculated and observed times, respectively, for ions to pass 121.4 cm. through a brass tube of 5.4 cm. diameter. Curves $B, B_1$; $C, C_1$; $D, D_1$ are plotted, using calculated and observed times for ions to pass 246 cm., 109 cm., and 25.4 cm., respectively, through a brass tube 2.95 cm. in diameter. For a brass tube 1.12 cm. in diameter, with the spark gap placed 226. cm. from the electroscope, for rates of flow greater than .25 cu. ft. per min. the difference between the calculated and observed times was less than .1 sec.

Sample decay curves are shown in Fig. 4. Observed times of passage of the ions through the tube were used as abscissæ rather than the times calculated by means of the meter from the rate of flow. Experimental conditions under which these curves were obtained are recorded in Table II.

The radium salt used in these experiments was contained in tiny aluminum tubes .7 mm. thick and approximately 2 cm. long. These were sealed into thin glass tubes to prevent leakage of radium emanation, and when used inside the brass tube were suspended at its axis by silk threads. The uranium cylinder referred to under *H* in Table II. was a hollow paper tube 5 cm. long and 2.9 cm. in diameter, with a coating of black oxide of uranium glued on the inside. This cylinder was suspended in the middle of the tube. The $\alpha$ radiation from uranium is so easily absorbed by air that the recombination constant obtained for this cylinder when placed in the tube of 2.95 diameter was .0099, a value evidently too large owing to the diffusion of the ions which were largely produced near the surface of the tube.

McClung[5] has shown that the recombination constant does not change with the pressure of the gas. Under the experimental arrangement of Fig. 2 the number of ions produced would change with the gas pressure and introduce a small correction for large capacities. Investigation showed that this change, if assumed to be linear, would be negligible for all capacities used.

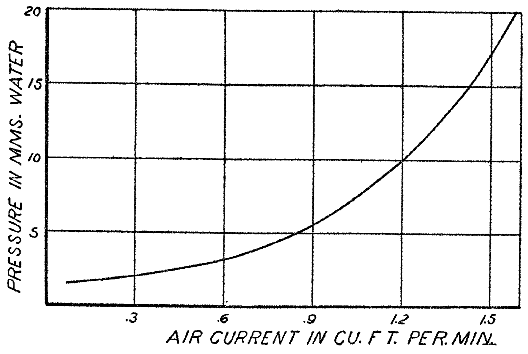

FIG. 5.

Fig. 5 shows the pressures in tube *B* for various air currents. The barometer reading was 75.35 cm. At 1.6 cu. ft. per min. the curve shows the correction to be .2 per cent.

Table III. contains the observed ionizations in divisions per minute for the above curves of Fig. 4, also the calculated values obtained

---

[5] *Loc. cit.*

TABLE III

| Curve | Vel. in Tube in Cm. per Sec. | Exp. Ionization in Divs. per Sec. | Calc. Ionization in Divs. per Min. | Recombination Constant: *α* |
|---|---|---|---|---|
| *A*..... | 42 | *40.9 | 41.1 | Mean value .0105 |
| | 28 | 38.0 | 38.4 | |
| | 22 | 35.8 | 35.6 | |
| | 16.5 | 32.8 | 32.5 | |
| | 14.0 | 30.8 | 30.4 | |
| | 12.5 | 29.8 | 29.2 | |
| *B*..... | 32 | *44.0 | 44.0 | .0107 |
| | 25 | 40.9 | 41.2 | |
| | 16.5 | *35.8 | 35.8 | |
| | 14 | 33.6 | 33.2 | |
| | 12 | 31.8 | 31.8 | |
| *C*..... | 30 | *121 | 121 | .0097 |
| | 24 | 94.5 | 89.0 | |
| | 19 | 83.4 | 79.3 | |
| | 17 | 76.5 | 75.7 | |
| | 16.5 | *65.5 | 65.5 | |
| | 14 | 53.0 | 59.8 | |
| *D*.... | 28 | *103.8 | 103.8 | .0081 |
| | 25 | 89.4 | 89.5 | |
| | 22 | 74.6 | 72.0 | |
| | 19 | *60.6 | 60.6 | |
| | 17 | 44.4 | 46.5 | |
| | 14 | 29.4 | 35.0 | |
| *E*..... | 47 | *79.8 | 79.8 | .0071 |
| | 45.3 | 74.8 | 74.4 | |
| | 27.6 | *64.0 | 64.0 | |
| | 20.7 | 59.5 | 58.5 | |
| | 13.8 | 53.0 | 57.7 | |
| *F*..... | 39 | *54.0 | 54.0 | .0094 |
| | 27.6 | 47.2 | 46.7 | |
| | 22 | *42.0 | 42.0 | |
| | 19.3 | 38.4 | 39.2 | |
| | 16.6 | 34.5 | 35.8 | |
| *G*..... | 30.4 | *105.5 | 105.5 | .0088 |
| | 24.8 | 69.0 | 65.5 | |
| | 19.4 | 44.5 | 43.0 | |
| | 16.6 | *32.4 | 32.4 | |
| *H*.... | 24.1 | *53.9 | 53.9 | .0057 |
| | 18.4 | 50.1 | 50.3 | |
| | 15.3 | 47.0 | 46.7 | |
| | 11.5 | 41.4 | 40.7 | |
| | 10.3 | *38.3 | 38.3 | |

by assuming the square law. The effect of diffusion at the lower velocities is well shown by the way in which the observed values fall below the corresponding calculated results. The values used in each experiment for calculating the recombination constant are marked by an asterisk.

In Table IV. the observed and calculated values are given for X-rays as an ionizing agent at a distance 27.7 cm. from the electroscope for an air current through a brass tube 2.95 cm. in diameter, using the arrangement of Fig. 1.

TABLE IV

| Vel. in Tube in Cm. per Sec. | Exp. Ionization in Divs. per Min. | Calc. Ionization in Divs. per Min. | Recombination Constant: *α* |
|---|---|---|---|
| 26.2 | *224 | 224 | .0099 |
| 22 | 182 | 182 | |
| 19 | 150 | 149.2 | |
| 16.6 | *121 | 121 | |
| 15.2 | 105 | 101 | |
| 14.0 | 90 | 98 | |

An attempt was made to see if the recombination constant was a function of the quality of a given radiation. X- or γ-rays were shot through the slit, first bare, then covered by foils or sheets of lead. A series of decay curves were thus obtained and the recombination constants calculated. Values were obtained with the slit bare at the beginning and end of the series to check the constancy of the sensibility of the gold leaf. The slit was covered at all times by a mica sheet .03 mm. thick.

TABLE V

| Thickness of Lead Over Slit | Vel. in Tube in Cm. per Sec. | Exp. Ionization in Divs. per Min. | Calc. Ionization in Divs. per Min. | Recombination Constant |
|---|---|---|---|---|
| Slit bare .... | 30.0 | *121.0 | 121.0 | .0097 |
| | 24.0 | 94.5 | 89.0 | |
| | 19.0 | 83.4 | 79.3 | |
| | 17.0 | 76.5 | 75.7 | |
| | 16.5 | *65.5 | 65.5 | |
| .15 mm...... | 27.6 | *76.0 | 76.0 | .012 |
| | 22.0 | 62.0 | 59.8 | |
| | 19.3 | 55.3 | 55.3 | |
| | 16.6 | *48.4 | 48.4 | |
| | 13.8 | 42.5 | 43.6 | |
| .20 mm...... | 30.0 | *79.6 | 79.6 | .0147 |
| | 27.6 | 72.4 | 71.3 | |
| | 20.7 | 54.0 | 55.0 | |
| | 16.6 | *43.0 | 43.0 | |
| | 13.8 | 37.3 | 39.5 | |
| .40 mm...... | 29.0 | *73.8 | 73.8 | .0164 |
| | 27.6 | 70.6 | 69.8 | |
| | 24.8 | 55.0 | 52.0 | |
| | 14.6 | *40.7 | 40.7 | |
| 1.2 mm...... | 27.6 | *64.0 | 64.0 | .019 |
| | 24.8 | 46.5 | 47.7 | |
| | 22.1 | 40.8 | 42.5 | |
| | 16.6 | *36.0 | 36.0 | |
| 2.4 mm...... | 27.6 | *53.7 | 53.7 | .0221 |
| | 22.1 | 42.2 | 40.0 | |
| | 19.3 | 37.0 | 36.1 | |
| | 16.6 | *30.8 | 30.8 | |
| Slit bare .... | 30.4 | *133.0 | 133.0 | .0096 |
| | 20.7 | 86.0 | 84.3 | |
| | 19.3 | 80.4 | 80.5 | |
| | 16.6 | *69.0 | 69.0 | |

Table V. contains the results of such a test for air as the source of ions in a brass tube of 2.95 cm. diameter and .300 mg. of radium salt as the ionizing agent placed at a distance 27.7 cm. from the electroscope and approximately 1 cm. above the slit.

TABLE VI

| Thickness of Lead Over Slit | Vel. in Tube in Cm. per Sec. | Exp. Ionization in Divs. per Min. | Calc. Ionization in Divs. per Min. | Recombination Constant: $\alpha$ |
|---|---|---|---|---|
| Slit bare..... | 24.8 | *210 | 210 | .0086 |
| | 19.4 | 150 | 156 | |
| | 16.6 | *121 | 121 | |
| | 15.2 | 105 | 108 | |
| | 13.8 | 90 | 102 | |
| .05 mm...... | 24.8 | *98.2 | 98.2 | .015 |
| | 19.4 | 68.0 | 68.0 | |
| | 15.2 | *46.2 | 46.2 | |
| | 13.8 | 40.1 | 42.6 | |

Table VI. gives results obtained for X-rays as ionizing agent, the slit being placed 27.7 cm. from the electroscope, with an air velocity in the brass tube of 2.95 cm. diameter. Table VII. records values for an X-ray ionizing source at 125.3 cm. from the electroscope, other experimental conditions remaining the same.

TABLE VII

| Thickness of Lead over Slit | Vel. in Tube in Cm. per Sec. | Exp. Ionization in Divs. per Min. | Calc. Ionization in Divs. per Min. | Recombination Constant: $\alpha$ |
|---|---|---|---|---|
| Slit bare..... | 30.4 | *105.5 | 105.5 | .0088 |
| | 24.8 | 69.0 | 65.5 | |
| | 19.4 | 44.5 | 43.0 | |
| | 16.6 | *32.4 | 32.4 | |
| .05 mm...... | 31.8 | *68.2 | 68.2 | .00923 |
| | 26.3 | 52.4 | 48.0 | |
| | 19.4 | *33.2 | 33.2 | |
| | 18.0 | 28.5 | 29.4 | |
| | 15.2 | 21.8 | 23.7 | |
| .1 mm ...... | 21.8 | *31.7 | 31.7 | .020 |
| | 26.3 | 24.7 | 26.7 | |
| | 23.5 | 20.3 | 20.2 | |
| | 18.0 | *14.9 | 14.9 | |
| | 16.6 | 13.8 | 13.5 | |
| Slit bare..... | 30.4 | *102.5 | 102.5 | .0080 |
| | 23.5 | 63.2 | 59.5 | |
| | 18.0 | *38.8 | 38.8 | |
| | 15.2 | 27.2 | 30.8 | |

The lack of saturation in the electroscope for large ionization currents would tend to give too small a value for the recombination constant, while diffusion effects at the smaller velocities through the tube would increase it. Neither of these causes, under the experimental conditions, would appear to be sufficient to explain the larger values obtained for the recombination constant for the more penetrating radiations.

I am indebted to the Providence Gas Co. for the gas meter which was used, also for its careful calibration before and after the experiments.

P. B. Perkins

Brown University,
June 28, 1917

## BOSTON MEETING OF THE AMERICAN CHEMICAL SOCIETY. III

### DIVISION OF BIOLOGICAL CHEMISTRY

C. L. Alsberg, *Chairman*

I. K. Phelps, *Vice-chairman and Secretary*

*The relation of the dissociation of hydrogen to enzymatic activity:* Howard T. Gräber and J. W. M. Bunker. It was demonstrated that the enzyme "pepsin," in agreement with the other enzymes, invertin and catalase, has an optimum at a definite H. ion concentration and that the presence of other ions exerts an influence which is not measurable, yet not negligible. It was shown that in the case of the weakly dissociated organic acids the buffer effect of the protein added has a marked effect upon the dissociation of the acids, but that when the concentration of the H ions was made equal to that of 3 per cent. HCl by considering temperature and protein the organic acids are equal to 3 per cent. HCl as activators for peptic digestion.

*On the origin of the humin formed by the acid hydrolysis of proteins III. Hydrolysis in the presence of aldehydes II. Hydrolyis in the presence of formaldehyde:* Ross Aiken Gortner and George E. Holm. Hydrolysis in the presence of formaldehyde completely alters the nitrogen distribution obtained by Van Slyke's method. Black insoluble humin is formed from tryptophane and no other known amino acid is concerned in the reaction. The primary reaction of black humin formation involves only the indole nucleus and not the $\alpha$ amino group of the aliphatic side chain of tryptophane. Formaldehyde forms a soluble humin with tyrosine which is precipitated by $Ca(OH)_2$. Hydrolysis in the presence of formaldehyde causes enormous increases in the ammonia fraction, but the increase is not due to ammonia, but to volatile