THE SO-CALLED POSITIVE PHOTO-ELECTRIC EMISSION (INVERSE EFFECT)

and

THE REALITY OF THE SUB-ELECTRON

by

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A THESIS
Submitted to the Faculty of
California Institute of Technology
in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

August 6, 1925

I. INTRODUCTION

A few observers have reported the discharge of positive electricity produced by ultra-violet light. Dember* found that a metal plate exposed to ultra-violet light in vacuum had the power to communicate a positive charge to a receiving cylinder when the proper accelerating field was applied. His experiments have recently been repeated by DuBridge,** who reports that Dember's results can be entirely accounted for on the basis of the photo-electric effect produced on the collecting cylinder by scattered ultra-violet light against which no precautions had been taken. His conclusions are "there is no measurable photo-electric production of either gaseous or metallic positive ions by the range of wave lengths emitted by the quartz mercury lamp.

R. Bär and F. Luchsinger*** working with small particles of paraffin and selenium in a Millikan electron apparatus found that some of the particles showed the inverse effect, that is, they became charged negatively when illuminated by ultra-violet light. This has been construed by some workers as indicating the discharge of positive electricity. However, as these men were only using the ultra-violet light to charge up their particles in order to measure the charge communicated, and were not interested in the source of the photo-electric effect it is natural to assume that no special precautions were taken against the light striking the metallic

*Dember, Ann. der Phys. 3, 137, 1909
**DuBridge, Phys. Rev., Feb. 1925, 201
***F. Luchsinger, Ar. Sc. Phys. et nat. 1, 544, 1919. R. Bär and F. Luchsinger, Phys. Zeit.,22, 227, 1921

plates of the condenser. The photo-electrons liberated from these metal surfaces being caught by the paraffin and selenium particles would make it seem as if the particles had lost a positive charge. S. Taubes*, working in the same laboratory as Luchsinger and Bär and presumably with the same apparatus, reported this inverse effect when dealing with particles that had a large positive charge and showed that it is due to the photo-electrons given off by the condenser plates, for when these were coated with paraffin the inverse effect entirely disappeared.

M. Hake**, working at Vienna and using a diminutive Millikan electron apparatus designed by Professor Ehrenhaft, has recently reported results on nineteen different materials. He found that metals show both the inverse and the normal effect, depending on the gas in which the metal particles are suspended, and that some insulators, for example glycerine, always show the inverse effect in all gases. Wasser***, working in the same laboratory as Hake gives results on mercury drops in N and CO_2. He claims that drops of larger radius than 1.9×10^{-5} always show the normal effect, that those between 1.1 and 1.9×10^{-5} cm. show both the normal and the inverse effect, while those of smaller radius than 1.1×10^{-5} cm. always show the inverse effect.

The following invewtigation was undertaken to test the correctness of the foregoing conclusions and to determine whether

*S. Taubes, Ann. der Phys. 6, 1925, page 646.
**M. Hake, Zeit. f. Phys. Band 15 Heft 2/3 1923
***E. Wasser, Zeit. f. Phys. Band 27 Heft 4, 1924

the changes in charge experienced by minute mercury droplets are of a magnitude corresponding to the electronic charge or to a charge smaller than this, as the Vienna physicists have maintained.*

II. METHOD

The apparatus used in the work consisted of a Millikan condenser such as has been used by Millikan and his pupils during the past fifteen years. Fig. 8, page 118 of "The Electron"**, by Millikan, shows a cross section. Fig 1 shows a diagramatic scheme of the apparatus. The illumination was pushed to its limit. The light which entered the window "g" was produced by a 500 c. p. Point-O-Light, the rays of which were concentrated by a powerful condensing lens. At 90° to this window was a quartz window through which a beam of ultra-violet light, which had been concentrated by a quartz lens and passed through the proper diaphrams so as to avoid striking the plates M and N, was allowed to pass. This ultra-violet light could be turned on and off by raising or lowering a shutter operated by a foot pedal.

The gases used were washed and filtered by slowly bubbling them through water, then through concentrated H_2SO_4, and finally passing them through a long tube filled with $CaCl_2$. The ends of the tube were plugged with glass wool. The nitrogen was also washed in a tower containing copper spinnings over which a solution of NH_4OH and NH_4Cl continuously passed. It was also bubbled through a bottle of strong KOH so as to remove any CO_2. Only three cubic centimeters per second passed; this gave the cleansing agents ample

*Phil. Mag., Vol xlix, Apr., 1925
**Rev. Ed., University of Chicago Press, 1924

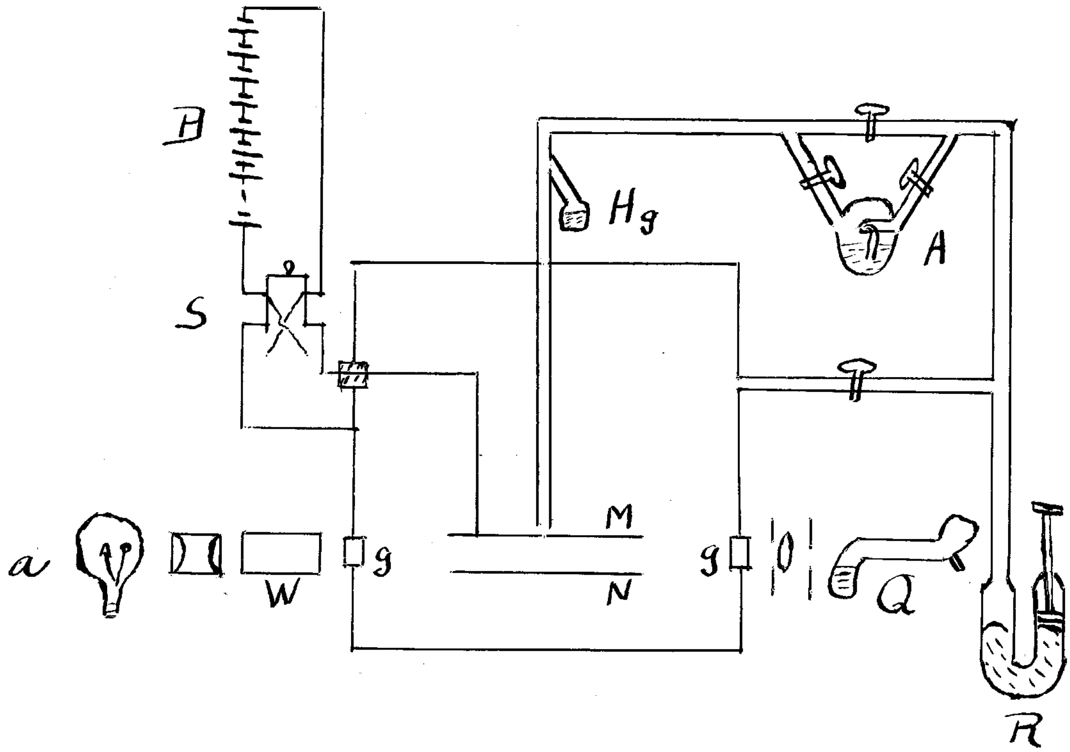


Fig I.

time to act.

In making observations the substance under test was blown over from the atomizer A by means of a mercury compressing device R which allowed the gas to be taken from the test chamber and returned through the atomizer without any danger of being contaminated. In the case of mercury the drops were produced by substituting the mercury boiler Hg for the atomizer A. When the drops of material were observed through the telescope the battery was connected. This caused the charged particles to be swept out of the field, leaving only the neutral ones. With the field still on the ultra-violet light was directed upon the drops and the speed observed with the battery first connected one way, then the other. In order to test whether or not the rays from the quartz lamp had the power of ionizing the gas, drops that were normally very sensitive were charged and held suspended in the field of view by connecting the proper battery. A narrow strip of opaque material was then placed across the quartz window so as to protect the drop from the direct influence of the ultra-violet light, but allow the gas on either side of the drop to be illuminated. With this arrangement prolonged exposure to the ultra-violet light, for ten minutes or more, produced no change in the charge of the drop, thus proving that the gas around it was not affected by the ultra-violet light.

III. QUALITATIVE RESULTS

Fifty drops of oil varying in apparent radius from 1.6 to 3×10^{-5} cm. were observed in air, N_2, H_2, CO_2, O_2, and He. <u>In no case was any effect observed.</u> <u>When the screens that kept the ultra-</u>

violet light off of the plates were removed, the inverse effect was immediately detected.

Fifty drops of glycerine of about the same range of diameters were observed in air, N_2, and H_2. In no case was it possible to detect any effect. The removal of the screens shielding the plates again produced the inverse effect.

A long series of experiments was conducted with Hg drops in air and in N_2. Fifty different drops of mercury, varying in apparent radius from 1.4 to 8.4×10^{-5} cm. were illuminated with ultra-violet light more than 80 different times when neutral and when charged with various charges, some times positive, some times negative. In no case was an increase of the negative or a decrease of the positive charge observed. Whenever a change occurred it was always of the normal type. The radii of these drops were computed by Millikan's* method. When Wasser's method is used they correspond to a range from .95 to 8.4×10^{-5} cm. Both methods use the assumption (shown below to be incorrect) that the density of all the particles is 13.6. They differ only in that Wasser's computations depend upon the assumption of a somewhat incorrect law of fall, while Millikan's method avoids this source of error. Wasser's range was from .7 to 3.3×10^{-5} cm. I have, therefore, worked over practically the same range of droplet-radii as did he.

Another method, and one which is, I think, an improvement upon the foregoing procedure, used by Wasser, was to charge the drops slightly by γ rays, and then adjust the applied potential so as to just balance the drop. In this way a single drop could be floated in

*Millikan, "The Electron", page 104

the field of view for 30 minutes or an hour at a time and thus the exposure time to the ultra-violet light increased. In no case was an inverse effect noted. Under this prolonged exposure to the ultra-violet light drops that were ordinarily classified as insensitive some times charged up in the normal way. When the screens that shielded the plates from the ultra-violet light were removed the drops showed the inverse effect after a very short exposure.

Our conclusions are that the inverse effect, reported by Hake and Wasser as indicating a discharge of positive electricity, has no real existence. It is a spurious effect produced by stray or scattered ultra-violet light striking the plates of the condenser and liberating photo-electrons which are caught by the drop in the apparatus. The correctness of this conclusion is suggested by the dimensions of Hake and Wasser's condenser, namely 9 x 9 x 2 millimeters. In such a condenser it is clearly extraordinarily difficult, if not altogether impossible, to make a concentrated beam of ultra-violet light pass through the 2 millimeter opening without its striking somewhere and scattering over the entire area of the plates. Our apparatus had the plates 15.3 mm. apart and was therefore better suited for testing the effect of letting the light strike the drop alone, the plates alone, or both.

IV. REALITY OF THE SUB ELECTRON

In the same region of radii in which Wasser finds that mercury droplets show the inverse photo-electric effect he also finds that the charge or change of charge on the droplets is far below the accepted value of the electron, that is, below 4.77×10^{-10} E. S. U.

In order to test whether or not changes of charge of smaller value than the electron are indeed ever produced by ultra-violet light, or otherwise, in drops of any size or kind a long series of experiments was carried out. My results are in agreement with Wasser's in that the apparent charges obtained on some of the drops, using Wasser's method of computing, fall below 4.77×10^{-10} E. S. U. But, the real test of the existence of the sub-electron in this experiment consists in finding whether all the charges obtainable on a given drop are exact multiples of the smallest charge which it is ever found to carry. Millikan* has emphasized this in one of his recent papers.

The justification for the foregoing statement is that Millikan and many other workers have shown that the smallest charge caught on an oil drop or any other kind of particle when ionization is produced in the surrounding gas is always 4.77×10^{-10} E. S. U. or some multiple of this unit irrespective of the size of the drop. If, then, when we are dealing with a mercury droplet we find that the charge given to it by an electron caught from the surrounding gas, which has been ionized by γ or x rays, is exactly the same as the charge given to it by being illuminated by ultra-violet light, it follows that the latter charge has also the value 4.77×10^{-10} E. S. U. Any contrary results obtained on the basis of an assumed density must per force be ascribed to a wrong assumption as to this drop-density.

In the accompanying Tables I, II, and III, $\frac{v_1 + v_2}{n}$ shows how perfectly the multiple relationship holds with precisely the same sort of drops used by Wasser and obtained under precisely the same

*Millikan, Phys. Rev. July 1925, page 101.

condition that he used when he thought he got sub-electrons by the photo-electric process. Table I shows results on a droplet that was very sensitive to ultra-violet light. Table II shows results on a drop that showed only slight sensitivity. The results in Table III were obtained with a drop that was not effected by the ultra-violet light even after several minutes exposure. These three tables are typical of results that were obtained on at least twenty-five different drops that were tested for multiple relationship, about half of them in air and half in pure nitrogen. Some of these drops were carried through twenty changes of charge. In no case was the variation of $\frac{v_1 + v_2}{n}$ more than 1.5% from the mean even though the readings were taken merely with a stop watch and therefore not with very great precision.

Here, then, we have the proof that the smallest quantity of electricity that any drop takes on is 4.77×10^{-10} E. S. U. and that it is independent both of the mechanism of charging and of the size of the drop. The reason for the apparent appearance of smaller charges in Wasser's and Ehrenhaft's work is shown in the following section.

V. SIZES AND DENSITIES OF DROPS

In calculating the radius of the drop the equation

$$a = \sqrt[3]{\frac{3Fen}{4\pi g(\sigma - \rho)} \frac{v_1}{v_1 + v_2}}$$

was used (Millikan, "The Electron", page 104). "e" was placed equal to 4.77×10^{-10} E. S. U. since the multiple relationship had established the fact that the charges were all unitary charges and since Millikan's work of the past fifteen years has fully established this value for the unit of charge. The results of this paper are, however, in no way different if a is computed from an approximate correction to Stoke's law and without any use of the value of e*. The method adopted is merely the more convenient and the more accurate. No drops were used on which sufficient data had not been obtained to establish the multiple relationship so that v_2, the velocity under a known field, could be established for a single electron on the drop. Wasser** uses for obtaining a the corrected form of Stoke's law of fall, namely,

$$\frac{4\pi a^3 \sigma g}{3} = \frac{6\pi a v_1 \eta}{1 + A\frac{l}{a}}$$

He assumes, however, that A is a constant. As a matter of fact, in the region of radii in which he thinks he works A varies from .7 to .98, as shown by Millikan***. While, however, Wasser's method and mine always agree quite closely for droplets which are actually spheres of mercury, his method yields apparent radii as much as 30% smaller than those given by my method for droplets which are not spheres of mercury. When calculated by Wasser's method our smaller drops are as small as those he uses. Either method, however, yields only the apparent size of the smaller drops as we shall show that the density of these is very far from that of Hg.

In order to find the charge on the drops, the value of e_1 was first found by means of the equation

$$e_1 = \frac{4\pi}{3}\left(\frac{9\eta}{2}\right)^{3/2}\left(\frac{1}{g(\sigma-\rho)}\right)^{1/2}\frac{(v_1+v_2)(v_1)^{1/2}}{F}$$

which is derived from the uncorrected form of Stoke's law.

*Professor Ehrenhaft is entirely in error in asserting that Millikan's results depend in any way upon the <u>assumption</u> either of a multiple relationship in drop-charges or a numerical value of e. These are both direct experimental facts. See Millikan, Phys. Rev., July, 1925, vol. 26, No. 1.

**Wasser, Zeit. f. Phys., Band 27, Heft 4, 1925, p. 207

***Millikan, Phys. Rev., 22, 1923

Then $e_1^{2/3}$ was plotted against 1/pa in the familiar Millikan*method. Fig. 2 shows the results obtained. The very sensitive, that is larger drops, fall on or close to Millikan's line, as shown in the figure, and give the correct value for e. The slightly sensitive and insensitive drops - these coincide with those which fall very slowly and hence for which a is apparently small - give low values for e and show no regularity in respect to position on the graph. In order to bring them upon Millikan's line it is necessary to assume for all these irregular drops densities much lower than that of mercury, - in the cases of some of them a density as low as one-ninth that of mercury. These are the droplets that Wasser assumes are pure mercury, although their densities are hereby shown to be as low as 1.5. Evidently he is working with an airy cluster of some kind.

This conclusion has recently been arrived at in Vienna itself by Mattauch, Ehrenhaft's assistant, who has determined the densities of these slowly falling droplets, obtained by condensing mercury. He has determined these densities by measuring the rate of fall of the same particle at two or more different pressures in nitrogen and has thus been able to make his computations independent of any use whatever of the charges carried by the drops. He, like myself, finds the densities of the most slowly falling of his drops to be between 1 and 2, instead of 13.6. <u>These results added to my own proof of the insensitivity of these drops to ultra-violet light of course show definitely that these slowly falling particles are not solid spheres of mercury</u>. The precautions which both Wasser and I have taken to obtain pure mercury are really of no significance for these experiments, first, because chemical methods of purifying mean

*Millikan, "The Electron", pages 91, 105.

nothing when such minute quantities of oxides or other impurities as are required to coat a few sub-microscopic particles are concerned, and second, because even if perfectly pure mercury be assumed there is nothing at all to show that pure mercury may not in the process of condensing some times form into clusters of particles so small that they might be insensitive to light of longer wave-length than 1800 A., such as Wasser and I have used. As Millikan has recently pointed out, the gaseous molecules of mercury have a long wave-length limit of about 1200 A., while liquid mercury has its long wave-length limit at 2735 A. How large the aggregate must be before the latter limit is reached, no one knows.

My results agree with Wasser in that the points in Fig. 2 may be divided into three regions; in the first of which the drops show only normal effect in ultra-violet light; in the second region some drops are sensitive in ultra-violet light and others are not, or only slightly so; in the third region all drops are insensitive. We agree, also, in that the slightly sensitive or insensitive drops are the ones that yield apparent values of "e" less than 4.77×10^{-10} E. S. U.

VI. VALUE OF THE CONSTANT A FOR Hg

The line drawn through those six points in Fig. II which, from data on their behavoir in ultra-violet light, we conclude to be pure mercury, gives $e = 4.77 \times 10^{-10}$. The value of the correction constant A in Stoke's law when calculated from the slope of this line is .695, a value in very good agreement with that obtained by Derieux*.

*Derieux, Phys. Rev., 11, 1918.

This is of theoretical interest as Millikan* has shown that in the generalized law of fall .7 is the lowest value that A can have, and corresponds to the case of diffuse reflection of gas molecules from the surface of the drop. It is also the lowest value that has ever been obtained for any material or that theoretically can be obtained.

VII. SUMMARY

The inverse photo-electric effect is a spurious effect and is not due to discharge of positive electricity. This has been proved by careful work on oil, glycerine, and mercury drops in various gases. Work with mercury drops shows that the drops that yield values of "e" smaller than 4.77×10^{-10} E. S. U. also show an abnormal behavior to ultra-violet light, that is, they are only slightly sensitive, or not sensitive at all.

The multiple relationship holds for the charges on these insensitive drops, proving that their charges are electronic and that it is erroneous to assume their density to be that of mercury.

Drops that are known to be pure mercury satisfy Millikan's $e_1^{2/3}$, $1/pa$ relation and yield 4.77×10^{-10} E. S. U. for the electronic charge, and .695 as the value of the correction constant, A, in Stoke's law.

*Millikan, loc. cit.

Table I

Sensitive Drop p 74 cm.

Change in charge produced by	Stop Watch Readings T_g	T_f	Average v_1	v_2	v_1+v_2	n	$\frac{v_1+v_2}{n}$
	47.0	24.5	.01120	.02171	.03291	-1	.0329
U. V. L.		24.2	"	.02194	.03314	+1	.0331
Spontaneous	47.1	9.4	"	.05553	.06673	+2	.0334
Spontaneous	47.4	23.9	"	.02226	.03346	+1	.0335
U. V. L.		9.4	"	.05553	.06673	+2	.0337
U. V. L.		4.3	"	.12372	.13492	+4	.0337
	48.3						

Volts	1925	a	2.3×10^{-5}
Distance between cross hairs	.532 cm.	e_1	7×10^{-10}
Distance between plates	1.53 cm.		

Table II

Slightly sensitive drop p 74.1 cm.

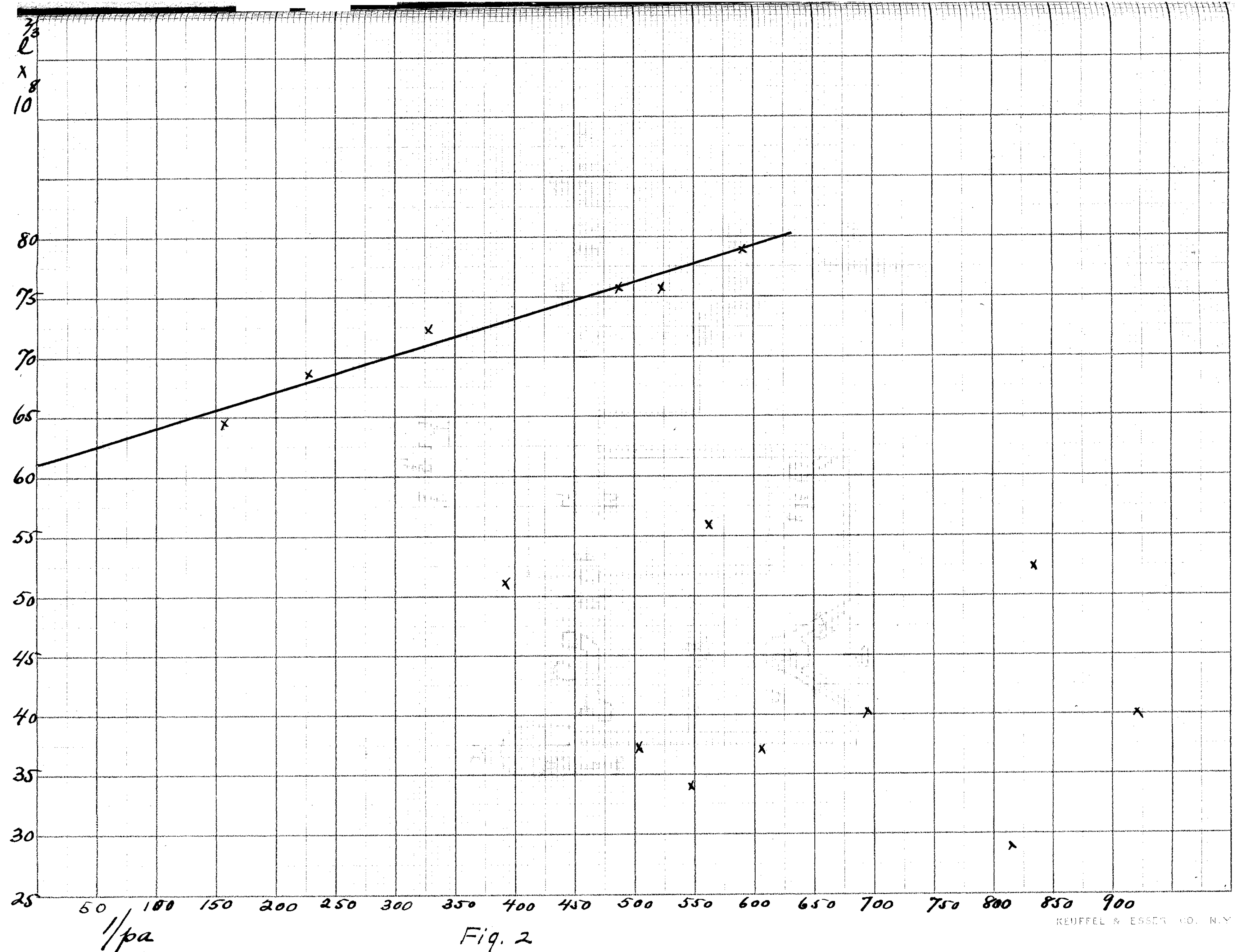
Change in charge produced by	Stop Watch Readings T_g	T_f	Average v_1	v_2	v_1+v_2	n	$\frac{v_1+v_2}{n}$
	63.2	4.2	.00841	.12666	.13507	-13	.0104
Spontaneous		9.7	"	.05484	.06325	-6	.0105
U. V. L.		12.1	"	.04396	.05237	-5	.0105
Spontaneous	64.0	15.9	"	.03325	.04166	-4	.0104
U. V. L.		42.0	"	.01266	.02107	-2	.0105
Spontaneous	61.6	242.0	"	.00219	.01060	-1	.0106

Volts	900	a	2.4×10^{-5}
Distance between cross hairs	.532 cm.	e_1	4.2×10^{-10}
Distance between plates	1.53 cm.		

Table III

Insensitive Drop p 74 cm.

Change in charge produced by	Stop Watch Readings Tg	Tf	Average v_1	v_2	$v_1 + v_2$	n	$\frac{v_1 + v_2}{n}$
		3.4	.00232	.15647	.15879	+6	.0264
Spontaneous	228.8	10.6	"	.05001	.05233	+2	.0262
Spontaneous	228.4	6.8	"	.07823	.08056	+3	.0268
Radium		21.9	"	.02429	.02661	+1	.0266
Radium		21.9	"	.02429	.02661	-1	.0266
Spontaneous	228.6	10.6	"	.05001	.05233	-2	.0262
Volts				1925		a	1.5×10^{-5}
Distance between cross hairs				.532 cm.		e_1	2.6×10^{-10}
Distance between plates				1.53 cm.			



$l^{2/3} \times 10^{8}$
80
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60
55
50
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35
30
25
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100
150
200
250
300
350
400
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500
550
600
650
700
750
800
850
900
1/pa

Fig. 2