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Probabilities of *K*-Electron Ionization of Silver by Cathode Rays

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K-electron ionization by impact is treated here both experimentally and theoretically. The experimental work is on Ag in extremely thin films bombarded by cathode rays from constant potentials up to seven times the minimum ionizing potential. Ratios of probabilities of K ionization at different voltages are found as ratios of K line intensities after the latter have been corrected for minor perturbing factors. One of these is the slight retardation of the cathode rays within the film. Another is the effect of cathode-ray diffusion, in increasing the numbers of atoms penetrated. These effects occur in all films. In some of our films, which were backed with Be, there were two more corrections, both for K ionization of the Ag by the Be: one through rediffusion of cathode rays into the Ag, the other through continuous-spectrum x-rays. Altogether, films without backing appear more reliable at high voltages, and films with it at low voltages, though when corrected as described, the results agree well at all voltages in the range covered. An approximate empirical formula is probability = constant $\times\, U^{-m} \log U$, where U is the ratio of tube voltage to minimum ionizing potential, and m is about 0.78. Among the theoretical formulas in the literature, those based on wave mechanics all depend on Born's approximation, which is invalid unless U is large, so they do not apply well to these data The classical quantum theory, considered as a possible temporary approximation, requires some further development, which is given here. The formula thus obtained seems to express the principles of classical quantum theory without seriously inaccurate approximations, but it agrees with the data only in the general type of the function: the ionization probability increases from zero at $U=1$ with a finite slope, attains a maximum value, and then declines. Quantitatively, the theory is far from the facts. A strictly heuristic modification of classical theory, changing the law of repulsion between the cathode ray and the K electron to an inverse cube, leads to a formula

$$\text{probability} = \frac{\text{constant}}{U\{(\pi/2 \cos^{-1} U^{-\frac{1}{2}})^2 - 1\}}.$$

This agrees fairly well with experiment, even though it contains no constant to change the shape of the graph, like the m in the other equation. But there is other evidence, as well as theoretical reason, for believing that the fundamental defect in the classical quantum theory lies not so much in any error in the inverse square law as in its dependence on contradictions of the uncertainty principle.

I. EXPERIMENTAL

A. Methods and apparatus

Regarding the above abstract as an introduction, we shall turn at once to the details of the experimental part of the research. Since the probability of ionization is to be studied as a function of the kinetic energy of a cathode ray, the first requirement is of course to have the same energy for all cathode rays in any one measurement, i.e., to use constant potentials. Up to about 100 kv these were obtained from a circuit of a type described previously by one of us[1] and shown in Fig. 1. Running on 500-cycle current, this gives a ripple of only about 4 volts

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[1] D. L. Webster, Proc. Nat. Acad. Sci. **6**, 26 and 269 (1920); D. L. Webster and A. E. Hennings, Phys. Rev. **21**, 301 (1923).

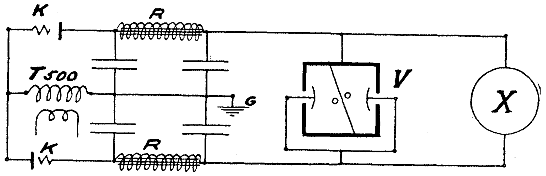

Fig 1.

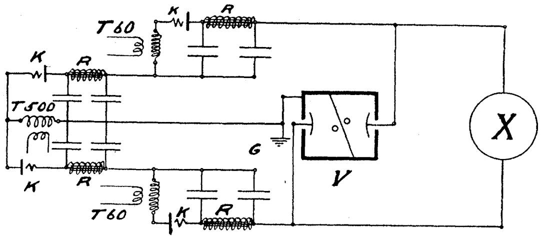

Fig 2.

Fig. 1. Circuit for use up to 100 kv. *T*500, 500 cycle transformer; *R*, reactors; *K*, kenotrons, *V*, voltmeter; *x*, x-ray tube.

Fig. 2. Circuit for use above 100 kv. *T*60, 60 cycle transformers.

at 10 m.a., as shown both by theory and by careful oscillograph measurements, for which we wish to thank Mr. H. E. Overacker, of the Department of Electrical Engineering.

Above 100 kv, we supplement this circuit with a pair of 60-cycle rectified circuits, as in Fig. 2. In adding such extra circuits, one must be very careful, on account of the oscillations of charges on the new transformers, because if these charges are drawn through the original circuit they will cause serious ripples. The preventive, of course, is very thorough electrostatic screening, not only around these transformers but between the coils of the insulation transformers feeding them, and also around the kenotrons and in their heating transformers, etc. With such screening the combined circuit is quite satisfactory, even though the flux leakage in the insulation transformers prevents the use of 500-cycle current in them and thus reduces the effectiveness of the filters. The resulting ripple at 200 kv, 1 m.a., is shown by Mr. Overacker's measurements to be about 50 volts.

Such lack of constancy as we have, therefore, is not primarily due to ripples but to slow irregular changes. These are minimized by running the 500-cycle generator and its d.c. exciter with a 3-phase motor sufficiently oversize to maintain a very constant speed at any load used. Up to 100 kv, therefore, the outfit is very steady indeed, though above 100 kv, the fluctuations of line voltage affect it through the 60-cycle transformers. Fortunately, however, the high tension voltmeter has a very short period, so that any variations of voltage due to such causes are easily detected. During every exposure of the ionization chamber to the rays, the voltage and tube current are carefully watched and controlled, the former through the field rheostat of the generator and the latter through a rheostat in the battery circuit that heats the filament. In this way up to 100 kv (that is, over the whole region of rapid change of line intensity), the variations of voltage are kept consistently less than 0.1 percent, and usually less than half that amount. For this tedious but very important part of the work, we wish to express most cordial thanks to Messrs. H. H. Baskerville, Jr., G. V. Webster, C. J. Burbank and A. W. Hackney.

The voltmeter referred to here is either of two that we have used, both designed by H. Clark. One, used for work up to 85 kv reported briefly in 1928,[2] was described in connection with earlier work on another problem.[3] The other, built for higher voltages, and used in all the later work, was described by Clark.[4] Both depend on bifilar suspensions of fine tungsten wires, and have shields around the insulators to prevent charges on them, which are unreliable, from affecting the suspended system. They are therefore very constant and reliable. They are calibrated with a series of 6 megohms of General Electric Company "copnic" voltmeter multipliers, and for the work since 1928 these have been surrounded by independently charged corona shields. Below 100 kv, the calibrations are direct; above that, the new meter is reconnected as described by Clark. These multipliers are themselves checked against standard resistances certified by the Bureau of Standards, and the current through them is measured on a Leeds and Northrup type *K* potentiometer, by using one of these standard resistances and a similarly certified standard cell.

Constant voltage gives uniformity of cathode-ray energy at the surface of the target, but for

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[2] D. L. Webster, H. Clark, R. M. Yeatman and W. W. Hansen, Proc. Nat. Acad. Sci. **14**, 679 (1928).

[3] D. L. Webster and A. E. Hennings, Phys. Rev. **21**, 312 (1923).

[4] H. Clark, Rev. Sci. Inst. **1**, 615 (1930).

uniformity at all the ionizing impacts one must also make the target extremely thin. For this purpose, in all the work reported in 1928[2] and in some of the later measurements, we used films of silver deposited on beryllium by rapid distillation in high vacuum. For two beryllium targets, in the form of cylinders with holes for cooling by circulating transil oil, we wish to express our cordial appreciation of the kindness and metallurgical skill of Mr. H. S. Cooper, of the Kemet Laboratories, Cleveland, Ohio.

A point of vital importance is that the films shall be uniform enough to contain no parts so thick as to increase unduly the corrections for retardation and diffusion of the cathode rays, mentioned above in the abstract. At high voltages, this means merely that the irregularities must be not over a thousand Angstroms or so, i.e., no worse than those of a mirror good enough to reflect normally incident light without appreciable scattering. These films satisfy this condition excellently.

As the tube voltage is reduced, both corrections are increased, and a need appears for more uniformity in the films. This need arises because each correction, when considered as a percentage of the x-ray intensity, is proportional to the thickness of the film so long as the film is uniform, but for an irregular film, this thickness is replaced by (mean square of the thickness)/(mean thickness).

The most exacting requirement for uniformity, however, is in the investigation of the fine structure of the ionization probability function very near the minimum ionizing potential V_K. One of the most definite predictions of the classical quantum theory of impacts is that this function, in its increase from zero at V_K, should start with its first derivative finite. Other quantitative predictions might be changed fairly readily by changing the assumptions about the laws of force, etc., but not this one. Presumably when the wave mechanics makes any prediction about the derivative at V_K, the data on it will furnish a crucial test of that theory also.

On the experimental side, the difficulty of getting these data in reliable form arises from the correction for retardation. A finite derivative for an ideally thin target, i.e., a monomolecular film, can readily be shown to produce a zero derivative for a target of finite thickness, but the converse does not follow. In fact, if the thick target probability, at any voltage V near V_K, is proportional to $(V-V_K)^n$, that of a thin target is proportional to $(V-V_K)^{n-1}$. A finite thin-target derivative at $V=V_K$ gives n a definite value, 2, but a zero thick-target derivative says nothing so definite. And any film thicker than monomolecular becomes a thick target when V gets near enough to V_K. The problem is to make practical thin targets such that the behavior of an ideal thin target can be deduced from intensities observed with them.

To see what this requires, let $i(U)\delta x$ denote the line intensity from an ideal target of strictly infinitesimal thickness δx, with $U=V/V_K$. Then with a real target of thickness X, neglecting the other corrections, the intensity is $X\overline{i(U')}$, where eV_KU' is the kinetic energy of a cathode ray retarded from eV_KU by going a distance x in silver, and the bar denotes an average from $x=0$ to $x=X$. Neglecting second-order terms, we obtain

$$U'=U+x(dU'/dx). \tag{1}$$

Then, approximately, so long as $U'>1$ even at $x=X$,

$$X\overline{i(U')}=Xi\left(U+\tfrac{1}{2}X\frac{dU'}{dx}\right)=Xi(U)+\tfrac{1}{2}X^2\frac{dU'}{dx}\frac{di}{dU}. \tag{2}$$

When $U'<1$ at $x=X$, of course, if di/dU is discontinuous at $U=1$, the second order terms become infinite and the whole theory must then be treated differently. Without going into detail, it is evident that the relation between the observed intensities and $Xi(U)$ is then of the type represented in Fig. 3. The test for a finite value of di/dU at $U=1$, so far as it can be made, is therefore to see whether an extrapolation like that shown in the dotted line of Fig. 3 strikes the potential axis with a finite slope; and if we had accurate data on dU'/dx we might add also a requirement that the intercept should be at the value of U noted in the figure.

If now the target is assumed to be nonuniform, the range of U over which the observed curve departs from the formula calculated above depends not on the mean thickness $\overline{X}$, but on the maximum $X_{\max}$ as indicated in Fig. 3. To make the extrapolation of Fig. 3 possible, $X_{\max}$ must be small enough so that this range of upward curvature will be restricted to a range of U lying well within the straight portion of the corrected intensity $Xi(U)$. Consider, for example, one of our films which had $X=280$A. The retardation in this distance at $U=1$ is only about 0.15 kv, at least as calculated from such data on dU'/dx as we have found in the literature. Therefore with $V_K=25.5$ kv, $XdU'/dx=0.006$. This is so small that we can readily allow $X_{\max}$ to be several times $\bar{X}$ without seriously impairing the test.

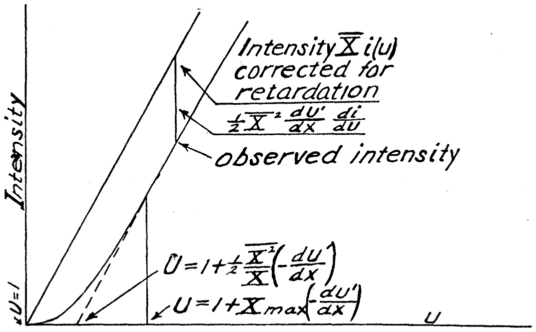

FIG. 3. Effect of retardation of cathode rays on intensities of x-rays near $U=1$.

To see whether $X_{\max}$ is within that limit, let us consider further the method of preparation of the films. The best way to secure uniform thickness was suggested to us by Joffé before our measurements of 1928, and later confirmed by the experiments of Reinders and Hamburger.[5] It is to keep the target cold with liquid air during the deposition of the film. The theory of this is that at room temperatures (at least if the real surface of the target is a nonmetallic adsorbed film) any lone silver atoms either migrate along the surface or re-evaporate; therefore permanent accumulation of silver starts only at the rare points where two lone atoms happen to come together before either of them re-evaporates. The silver that accumulates is then in the form of crystals growing around these points. At liquid air temperature, on the contrary, migration and re-evaporation are prevented, and the silver accumulates everywhere into a smooth film. Nevertheless, we were reluctant to subject our beryllium targets to such sudden changes of temperature as in using liquid air. Experimenting on copper targets first, therefore, we found that slow deposition, by sublimation from silver wires kept just below their melting point, gave matt surfaces, easily resolved by a microscope into glittering silver crystals. On the other hand, distillation from molten silver in a molybdenum trough, several hundred degrees hotter, gave perfect mirrors, especially if the trough had previously been heated in hydrogen to clean the molybdenum and silver and make good thermal contact between them. All this is exactly as expected from the above theory. We believe, therefore, that in using rapid distillation (20 to 50A thickness per second) we accomplish something of the same objective as with a cold target.

As to how uniform these films are, one line of evidence is the practically complete disappearance of the color of copper with about 50A of silver and perfectly complete with 100, which may perhaps mean complete covering of the copper surface at such thicknesses. For comparison, we have 45A, given by Reinders and Hamburger as the thickness needed for appreciable electrical conductivity in silver films on glass made by sublimation at room temperature. At 400A such films attain the very high conductivity of massive silver. This implies for 400A, not only complete connections between crystals, but also a fair approximation to the uniformity of thickness required for a minimum of resistance. Altogether it seems reasonable to assume that with fast distillation we probably had deposition practically everywhere by the time the mean thickness was 50 or 100A. From there on, as indicated by Reinders and Hamburger's theory of deposition, there should be no appreciable increase in the sizes of the irregularities. In studying the fine structure of the excitation function, therefore, we shall assume that all of these films, both those of our 1928 paper[2] and later ones, had their maximum thicknesses within a very few hundred Angstroms of their averages.

At some of our higher voltages, as noted above, we used not only silver films on beryllium, but

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[5] W. Reinders and L. Hamburger, Ann. d. Physik **10**, 649 and 668 (1931); Hamburger, ibid. **10**, 789 and 905 (1931), and **11**, 40 (1931).

also other films, of silver leaf about 1800A thick, with no backing. This leaf, of course, was far from uniform, obviously porous in a strong light, and not a perfect mirror. Fortunately, however, we do not need to rely on it except at voltages so high that it can be very non-uniform without serious error.

The measurement of thickness of thin silver films can be accomplished in either of two ways. One is by the use of x-rays from a standard Coolidge tube. If these rays are sent through the film, their spectrum is given a discontinuity at the *K* limit of silver, and the thickness of the film can be found from the magnitude of this discontinuity. Practically, to make it show strongly enough with a film only a few hundred Angstroms thick, the rays must go through the films very obliquely, say at about 3°. With silver leaf, on the other hand, one may use 10 sheets or so with normal incidence. The other method of measurement is by comparison of intensities of line rays, between the thin film and a thick target, as explained in our 1928 paper. For the thickest film used then, 280A, these methods agreed as noted there, far better than one might expect. For the silver leaf used recently, 10 sheets measured by absorption gave a mean thickness of 1770A, whereas 3 measured the other way gave 1900, 1650 and 1700A according to our formulas of 1928. For the thinner films, both methods are very inaccurate, but for the thicker films the absorption method is preferable because of the uncertainties as to cathode-ray retardation involved in the other method. We are therefore basing our estimates of thickness primarily on the absorption in these thickest films, and thinner ones are estimated by ratios of their line intensities to a mean of those of the three silver leaf films.

So much for the problem of uniformity of kinetic energy of impacts. A matter of equal importance in studying any ionization probability as a function of voltage is to insure that the number of cathode rays striking the film per second shall be the same at all voltages. For our 1928 work, we approximated this condition well up to 65 or 70 kv with a tube much like a standard Coolidge tube except that the electrodes were demountable and that it was pumped during operation. (Mercury vapor was kept off the films at other times by a cock in the vacuum line at the top of the liquid air trap.) At higher voltages, however, keeping the power down to 50 watts, to retard the disintegration of the brittle beryllium targets, serious difficulties arose from field-current and positive-ion effects. To overcome these and obtain a satisfactory technique for intensity measurements at high voltages with small currents, we developed a new type of tube, described in detail in the *Review of Scientific Instruments*.[6]

To the treatment of the general problem of such measurements given there, we need add only some details on the special anodes used here. For films on beryllium, the anode was a simple cylinder, oil cooled inside, with a flat end for the target, 21 mm in diameter, perpendicular to the axis. The cathode rays struck this end normally, on a focus 6 mm in diameter, expanding to 8 mm in very much overexposed pinhole pictures, but never more; and this focus was centered to within 1 mm, so as to eliminate any danger of losing cathode rays beyond the edge of the target. To catch rediffused electrons, we mounted a cylindrical steel fence, of inside diameter equal to the diameter of the target, and of length 12 mm, coaxially with the target, with its nearer edge 5 mm in front of the target. While this fence is not of vital importance, it helps to insure accuracy in our rediffusion correction by catching most of the rediffused electrons and preventing them from being attracted back to the target face.

For using silver films without the beryllium backing, we mounted them on the end of a hollow cylinder, or tube, 21 mm o.d. like the beryllium target, and 16 mm i.d. In front of the film, to prevent the electrostatic field from tearing it to pieces, were two grids of 0.1 mm tungsten wires, threaded through holes in a sleeve that fitted over the cylinder holding the film. Two such holders were used. The first, made of copper, had the cylinder bored to a depth of 29 mm. The second was made of aluminum, to be more nearly free from rediffused rays from the bottom of the hole, and was 63 mm deep. The films were stretched very flat, giving them almost no freedom of motion and insuring

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[6] D. L. Webster, W. W. Hansen and F. B. Duveneck, Rev. Sci. Inst. 3, 729 (1932).

against wrinkles that would allow any x-rays going to the spectrometer (at 5° from the plane of the film) to suffer serious absorption.

The spectrometer is of the Bragg type, with a Seemann slit, used with the familiar precautions against errors due to changes of size or position of the cathode-ray focus. The main point here, of course, is to have all slits wide enough to include all the rays of either line of the $K\alpha$ doublet that will reflect from the crystal when it is set for the line measurement. Incidentally, the range of continuous spectrum should be limited by only one slit, the one we use for this purpose being the Seemann slit. To minimize the deduction for continuous spectrum rays, this slit is made as narrow as is consistent with certainty of including all the line rays.

The only new feature of this spectrometer is the ionization chamber, which was made in two compartments with opposing potentials to cancel natural ionization, only one compartment being exposed to the x-rays. The slight residual effect due to unavoidable inequalities is cancelled by a collector of natural ions in the pipe carrying the wire to the electrometer. Since all compensation here depends on natural ionization, this apparatus is better than the usual radium-compensated chambers, in being much less sensitive to changes in the emanation content of the air around it.

The electrometer was of the Compton type, used ballistically as explained elsewhere.[7] It was checked often with a potentiometer, to make sure there were no departures from linearity greater than one percent, and corrections were made for such departures as there were. In short exposures of the chamber to the rays, such as 10 or 20 seconds, as used with silver on beryllium, a group of electrometer readings at one setting would usually give a mean deviation of individual readings of about 0.3 percent. Deducting the continuous spectrum, the mean deviation in a line intensity measurement would be relatively greater, ranging from about 1 percent, in the neighborhood of $U=2$, to 2 or 3 percent near $U=7$. With silver leaf, the tube current had to be limited to 40 microamperes or less, giving weaker rays and requiring longer exposures, usually 60 seconds. These gave more chance for errors from zero shifts, unbalanced fluctuations of natural ionization, etc., but the deduction for the continuous spectrum was much less. So here also, 2 or 3 percent is a fair estimate for the errors.

The deduction of the continuous-spectrum intensity just mentioned can be made in either of two ways. The most obvious, graphical interpolation, was used with our first 5 films, in our work up to 85 kv reported briefly in 1928. More recently, however, we have used an analytical method, depending on a Taylor's series for the continuous spectrum intensity about the α-line glancing angle θ_α. (This angle is the middle of the short flat top of the peak given by the slit width conditions described above.) Writing the series as

$$I(\theta)=I(\theta_\alpha)+c_1(\theta-\theta_\alpha)+c_2(\theta-\theta_\alpha)^2+\cdots, \quad (3)$$

we apply it to 5 angles, equally spaced with an interval $\theta_1=0°\ 13.5'$. These angles, taken in increasing order, will be called θ_{-2}, θ_{-1}, θ_α, θ_{+1}, θ_{+2}.

A simple linear interpolation, $\frac{1}{2}\{I(\theta_{-1})+I(\theta_{+1})\}$, is sufficient for use with the silver leaf targets without backing, because with them the continuous spectrum is very weak. With films on beryllium, however, it is definitely incorrect if (as is usually the case) the graph of the spectrum is appreciably curved at θ_α, i.e., if the quadratic term in the series is appreciable. The next approximation, covering both the quadratic and cubic terms, is obtained by adding to the first $(1/6)\{I(\theta_{-1})+I(\theta_{+1})-I(\theta_{-2})-I(\theta_{+2})\}$. This is sufficiently accurate for all practical purposes, as shown by tests with a bare beryllium target, and probably at least as accurate as the graphical method, as well as faster—an important advantage when using perishable targets.

B. Data

Measurements were made with thirteen films, denoted here by letters *a* to *m*, the first nine being silver on beryllium and the last four free silver leaf. Films *a* to *e* were made by successive depositions of silver, with care never to touch the surface. Each one therefore included those before it, though films *a* to *d* were used so little that film *e* was practically fresh when first put to use. This film, however, was used for a long series of measurements, and then the tube was dismantled

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[7] D. L. Webster, and R. M. Yeatman, J. O. S. A. and R. S. I. **17**, 248 (1928).

and work was started on a tube for higher voltages. Before the beryllium target was used again, therefore, the silver was removed with cyanide and the surface was ground down on a lathe, far enough to remove any minute pits into which the silver might be rubbed in cleaning. Then it was polished and tested for silver K radiation, of which no trace could be found. Then film f was deposited and used, and the same process was repeated. Film i was on a new beryllium target.

While the data from all the films were consistent, they differed in accuracy for various reasons, and we are therefore discarding the less accurate ones. These include: films a, b, c, g, which were too thin to give rays as intense as were desirable; film h, which was marred by transil oil seeping through a crack in the beryllium target; and film j, the first silver leaf without any backing, which got torn too soon to give a comparison of intensities at different voltages. The films retained differ considerably in the values of the corrections they need, and the data on which the corrections are based are not so good as we may hope for later. We are therefore presenting the most essential data here without any corrections, for use at any time when the corrections can be calculated more exactly than now.

To make the data on different films comparable, in spite of different thicknesses and different adjustments of the electrometer and other instruments, it is desirable to express all intensities for each film in terms of the intensity for that film at a standard voltage. For this we have chosen $U=2$, the integer giving a higher efficiency of line-ray emission than any other, and so giving the greatest accuracy with films on beryllium. Intensities reduced to this standard will be denoted by $j(U)$, to distinguish them from $i(U)$, the absolute intensity per unit film thickness mentioned above.

Two minor points about this reduction should be mentioned. One relates to films d and e, for which data were not taken at exactly the voltages listed here, on which most of the work on later films was concentrated. The values for d and e were therefore obtained by graphical interpolation from a graph of $(\log U)/j(U)$ against U, like that of Fig. 5, below. Values given in parentheses are inaccurate because of stray currents at the highest voltages in the tube used in 1928.

The observed intensities, reduced in this way, are given in Table I.

TABLE I. *Observed intensities, reduced to* $j(U)$.

U	*On Beryllium*				*Free Leaf*, 1932–33		
	In glass bulb tube, 1928		In steel and Pyrex tube, 1932		Copper holder	Aluminum holder	
	d, 170A	*e*, 280	*f*, 450	*i*, 1400	*k*, 1900	*l*, 1650	*m*, 1700
1.2	0.39	0.394	0.401	0.418		0.387	
1.5	0.73	0.714	0.732	0.781		0.760	
2.5	1.12	1.115	1.110	1.084		1.070	
3.0	(1.16)	(1.16)	1.176	1.110		1.078	1.074
3.5			1.203	1.116		1.079	
4			1.203	1.125	1.070	1.068	1.062
5			1.210	1.103	1.043	1.037	1.036
6			1.212	1.103	1.023	1.005	0.987
7			1.193	1.107	1.002	0.967	0.972

C. Corrections

As noted above, all these films must be corrected for such systematic errors as are inherent in the diffusion and retardation of cathode rays in any thin film. Furthermore the films on beryllium and the one on the copper holder must be corrected to eliminate the x-rays produced by cathode rays striking the films for a second time because of rediffusion. And those on beryllium need still a fourth correction, to eliminate fluorescence of the film under x-rays from the beryllium.

Two of these corrections, those for diffusion within the film and rediffusion from the beryllium, have been treated at length in a previous paper.[8] The effect of diffusion is to make each cathode ray, in its passage through the film, take a curved path and thereby go through more atoms than it would if it went straight. For a film of uniform thickness X_0, the mean length of path is a function of U which we call $X(U)$. For absolute intensities, if we could measure them, the correction would consist in multiplying the observed intensities by $X_0/X(U)$. For relative intensities reduced to unity at $U=2$, the correction factor is $X(2)/X(U)$, which we shall call c_d', the correction for diffusion.

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[8] D. L. Webster, H. Clark and W. W. Hansen, Phys. Rev. **37**, 115 (1931).

The calculation of $X(U)$ involves several approximations of the type sec $\theta = 1 + \theta^2/2$, which is nearly one percent low at $\theta = 25°$, or sec $\theta = 1.10$. Taking these approximations altogether, the error in $X(U)/X_0$ at any given value, such as this 1.10, may be two or three times as large as that in sec θ at the same value. This makes the values of c_d for our thicker films at low voltages very uncertain. In tabulating them we are therefore using parentheses to indicate probable errors of 5 or 10 percent in $X(U)/X_0$, and square brackets for figures even more unreliable. At high voltages, however, since the excess of $X(U)/X_0$ over unity varies nearly as U^{-2}, the error in $X(U)/X_0$ decreases rapidly. c_d then approaches $X(2)/X_0$, keeping only such constant error as there may be in this ratio. The ratio of c_d at $U = 4$ to that at $U = 7$, for example, must be free from any serious error. With these reservations, the values of c_d are listed in Table II.

TABLE II. *100*(c_d–*1*).

	On Beryllium				*Free Leaf*		
U	*d*, 170A	*e*, 280	*f*, 450	*i*, 1400	*k*, 1900	*l*, 1650	*m*, 1700
1.2	−1.7	−2.9	−4.7	[−12.4]		[−14.0]	
1.5	−0.7	−1.5	−2.3	(−5.7)		(−7.3)	
2.5	+0.5	+0.7	+1.0	+3.2		+3.7	
3.0	+0.8	1.1	1.6	5.7		6.2	6.4
3.5			2.0	6.3		7.4	
4			2.2	7.1	9.5	8.2	8.5
5			2.5	8.1	10.9	9.4	9.7
6			2.7	8.7	11.7	10.2	10.5
7			2.8	9.0	12.2	10.5	10.8

The rediffusion correction also is calculated as in our paper of 1931,[9] but with changes for more recent data on rediffusion, found by Neher.[10] Such data as were previously available had indicated that the rediffused electrons probably departed notably in their directional distribution from the simple cosine law. But Neher's data (both those in the abstract cited and others very kindly furnished us by letter) prove these departures to be actually too small to consider. In the formulas derived in our previous paper, this changes a factor called S from 2.11 to 2.00. A more important effect of Neher's data is on the value to be adopted for the so-called rediffusion constant, p. Data previously available were all on elements from aluminum to gold, for which p is practically independent of U, and extrapolation had indicated for beryllium a value $p = 0.043$. Neher, however, found for beryllium 0.029 at 70 kv and 0.025 at 130, with intermediate values between. For extreme accuracy, this dependence on voltage should produce some changes in the method of calculating the correction to our data. Practically, however, since the correction is small anyway, and these changes all reduce it still further, it is sufficient for the degree of accuracy attainable to date to assume $p = 0.025$. In the final values of the correction, p and S enter only in their product, which is thus changed from 0.090 to 0.050.

In our previous paper, there was considerable uncertainty in the energy distribution function for the rediffused electrons, but calculations with several alternative functions showed that changes could be made over a wide range without seriously affecting the result. It is therefore of interest to note that new data by Chylinski[11] on silver confirm the idea that this distribution function is within the range considered. These functions were of two types, chosen for integrability in connection with two empirical intensity formulas. The latter were almost equally good up to $U = 3.3$, our limit in 1928, but one of them fails at higher voltages. The present corrections are therefore extended to $U = 7$ on the basis of the other one, that the line intensity is

$$i(U) = \text{const} \times U^{-0.8} \log U. \tag{4}$$

With the free films, not on beryllium, one cannot entirely neglect rediffusion, because the cathode rays must eventually strike something, and some of them can then rediffuse to the film. The first apparatus we used to hold such films, as described above, was made of copper. For this, calculations based on the cosine law of distribution and a value of 0.29 for the rediffusion constant of copper show this correction to be 0.9 as large as for films on beryllium. But with the aluminum holder used later, this factor is reduced to 0.1, making the correction negligible.

These corrections, with $pS = 0.050$, are given in

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[9] D. L. Webster, H. Clark and W. W. Hansen, Phys. Rev. **37**, 115 (1931).

[10] H. V. Neher, Phys. Rev. **37**, 655 (1931).

[11] S. Chylinski, Phys. Rev. **42**, 393 (1932).

Table III in terms of the factor c_r, by which the intensities must be multiplied to correct for rediffusion, still keeping the intensity at $U=2$ unity.

TABLE III. $100(c_r-1)$.

	On Beryllium	*Free Leaf*	
U	films d, e, f, i	On copper holder film k	On aluminum holder films l and m
1.2	+1.6	+1.4	+0.2
1.5	+1.0	+0.9	+0.1
2.5	−0.7	−0.6	−0.1
3.0	−1.2	−1.1	−0.1
3.5	−1.6	−1.4	−0.2
4	−1.9	−1.7	−0.2
5	−2.2	−2.0	−0.2
6	−2.4	−2.2	−0.2
7	−2.6	−2.3	−0.3

Turning now to the correction for retardation of the cathode rays, the main principles of this have already been stated in connection with the preparation of films, in Section IA. By Eq. (2) there, it can obviously be put into the form of a factor c_x like c_d and c_r, above, as soon as we have approximate data on $i(U)$, di/dU and dU'/dx. For the first two of these functions, the uncorrected data of Table I are sufficient, or one may use the empirical Eq. (4), above, which readily gives

$$c_x=[1+Xf(2)]/[1+Xf(U)], \tag{5}$$

where X is the thickness of the film and

$$f(U)=\tfrac{1}{2}(dU'/dx)_{U'=U}U^{-1}\{-0.8+(\log U)^{-1}\}. \tag{6}$$

For dU'/dx, the data in the literature are somewhat contradictory, but it seems to us best to use an empirical equation found by Williams[17] for light elements, modifying it slightly. In our notation, it is

$$V_K(dU'/dx)=-a\rho\beta^{-1.4} \tag{7}$$

where $\beta=v/c$ as usual, ρ is the density, and a is a nearly constant factor a few percent over 1.06 kv cm^2/g. We shall take the numeric of a to be 1.1.

One modification needed for heavy elements, since retardation is done only by extranuclear electrons, is the insertion of a factor $2Z/A$, where Z and A are the atomic number and weight. This is probably not a sufficient change, since it weights all electrons alike and the tightly bound K and L electrons of silver should not be counted in full; but it is probably good enough for the present purpose.

Another modification, for convenience, is the approximation, good within 15 percent over our range of voltages, that

$$U=(\beta/\beta_K)^{2.5}. \tag{8}$$

Together, these lead to

$$dU'/dx=-(2.1\times 10^3\ \mathrm{cm}^{-1})\,U'^{-0.56}. \tag{9}$$

With these equations, we find corrections for our films as shown in Table IV.

TABLE IV. $100(c_x-1)$.

U	d, 170A	e, 280	f, 450	i, 1400	k, 1900	l, 1650	m, 1700
1.2	+0.6	+1.0	+1.6	+5.0		+5.9	
1.5	+0.1	+0.2	+0.3	+1.0		+1.2	
2.5	0.0	0.0	−0.1	−0.2		−0.3	
3.0	0.0	0.0	−0.1	−0.3	−0.4	−0.3	−0.3
5			−0.1	−0.3	−0.5	−0.4	−0.4
7			−0.1	−0.3	−0.5	−0.4	−0.4

Only one correction remains; namely, that for fluorescence of the silver films on beryllium, under continuous-spectrum x-rays from the beryllium. In our 1928 paper, we estimated values for that on the basis of equations taken from an earlier paper,[12] on thick silver, in which rays produced directly by impact ionization were compared with those produced indirectly by fluorescence. The latter were calculated by integration with respect to depth into the target. For silver films on beryllium, we took the integrand of this integral, multiplied it by the thickness of the films, and multiplied it also by 4/47 on the assumption that the continuous-spectrum rays causing the fluorescence would be simply proportional in intensity to the atomic number of the element they come from.

This assumption may hold well enough for rays emerging at large angles from the face of the target, but at small angles it is incorrect, because of absorption in the target. Although this error becomes notable only below about 5° or so, it is at exactly such angles that the silver film can absorb the largest fraction of the rays. Changing to a more detailed calculation, therefore, the fluorescence correction is increased by an un-

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[12] D. L. Webster, Proc. Nat. Acad. Sci. 4, 330 (1928).

expectedly large factor, becoming for high voltages the largest of the four corrections. It was on this account that we decided to supplement our data on films on beryllium with others on free films, at least for high voltages; and it was primarily this change in the fluorescence correction, rather than any difference between the new data and the old, that necessitated a revision of our intensity values between two recent abstracts.[13]

The integral for the intensity of fluorescent rays, assuming the film to be of infinite area, is

$$X_0 f(U)=\tfrac{1}{2}\int_{\nu_K}^{\nu_0}\int_0^{\pi/2} I(\nu_0,\,\nu)(1-e^{-\mu X_0 \sec\theta})\frac{\mu_K}{\mu}\cdot\frac{\nu_\alpha}{\nu}\,u_\alpha \sin\theta d\theta d\nu. \tag{10}$$

Here $I(\nu_0, \nu)d\nu$ is the intensity of the beryllium spectrum in the range $d\nu$, in directions perpendicular to the cathode rays (other directions counting but little), ν_0 is the high-frequency limit, and ν_K the K limit of silver. μ is the absorption coefficient of silver at frequency ν, and μ_K the part of it due to K electrons. θ is the angle made by any ray with the normal to the target. u_α is the fluorescence yield of silver for its α-lines only.

For values of these quantities, we take μ and μ_K to be proportional to ν^{-3}, using Richtmyer's[14] values at the K limit. For u_α, we use Balderston's[15] value 0.62.

For $I(\nu_0, \nu)$ a first approximation is to call it simply proportional to $(\nu_0-\nu)$. This is in line with measurements by Wagner and Kulenkampff[16] on many elements up to 12 kv, and by Webster and Hennings[3] on molybdenum up to 70 kv, and it yields a quickly converging series for $f(U)$. But special measurements to test it here indicate that it is considerably in error at high values of ν_0/ν, the graphs of $I(\nu_0, \nu)$ against ν_0 being concave downward. To correct for this, we have plotted several such graphs for various values of ν, and modified the corrections according to them arithmetically. Fortunately, the region fairly near ν_K contributes nearly all the fluorescence rays, even at high voltages. Therefore, while we cannot claim great accuracy for it, without any direct test of $I(\nu_0, \nu)$ as a function of ν, it is probably much more accurate when calculated this way than by the simple linear formula.

Another correction to this integral is for the fact that the depths of production of the beryllium rays at high voltages are not strictly infinitesimal in comparison to the radius of the target, 10.5 mm, so the target cannot be considered as of infinite extent. At $U=7$, for example, the extreme case, Williams's[17] retardation formula for cathode rays shows a range of 0.030 mm. At half this depth, however, Bothe's[18] diffusion formula shows a most probable angle of deviation just over one radian. So the mean depth of production of x-rays will not be half the range, but something nearer a third of it. Even this, however, is appreciable, on account of the sec θ in Eq. (10), and it requires a change in the limit of integration with respect to θ, from $\pi/2$ to the angle for rays going to the edge of the target.

To use the fluorescence intensity thus calculated for correction of the line intensity, the essential point to note is that it is expressed in terms of the continuous-spectrum intensity from beryllium. It can therefore be related directly to the observed continuous intensity at the silver lines. One must of course take proper account of the fact that the ratio of electrometer readings for line and continuous rays depends on the resolving power of the spectrometer. This is easily done, however, by using the ratio of the area of the line, plotted on any scale, to the ordinate in the continuous spectrum under it, this ratio being independent of resolving power.

Altogether, this correction is not only arithmetically cumbersome but at high voltages the least accurate of the four. In tabulating it, therefore, we are indicating relatively large probable errors by parentheses. The values, in a

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[13] D. L. Webster, W. W. Hansen and F. B. Duveneck, Phys. Rev. **42**, 141L (1932) and **43**, 384A (1933).

[14] F. K. Richtmyer, Phys. Rev. **27**, 1 (1926).

[15] M. Bladerston, Phys. Rev. **27**, 696 (1926).

[16] E. Wagner and H. Kulenkampff, Phys. Zeits. **23**, 503 (1922).

[17] E. J. Williams, Proc. Roy. Soc. **A130**, 310 (1932).

[18] W. Bothe, Handbuch der Physik **XXIV**, 18 (1927).

form analogous to that used for the other corrections, are in Table V.

TABLE V. $100(c_f-1)$.

U	d	e	f	i
1.2	+2.8	+2.8	+2.7	+2.0
1.5	+2.1	+2.0	+1.7	+1.4
2.5	−1.1	−1.1	−1.2	−1.2
3.0	−2.8	−2.6	−2.5	−2.5
3.5			−3.7	−3.7
4			−5.0	−4.9
5			(−7)	(−7)
6			(−9)	(−8)
7			[−11]	[−10]

D. Results

These corrections are now applied to the data of Table I. The results are tabulated for the individual films in Table VI and then averaged in the last column, "weighted average."

The weighting here is based on various considerations. These include of course the numbers of measurements at each point, and also questions of reliability, on the basis of which, for example, the data of 1928 at the highest voltages used then are discarded entirely because of stray currents in the tube. A further question of reliability relates to the corrections, especially those for fluorescence, which is large and unreliable at high voltages, and for diffusion, which becomes unreliable at low voltages in thick films. On this basis we favor the free silver leaf films at high voltages and the films on beryllium at low. However, these questions of judgment are not of primary importance, because the data of both types agree fairly well anyway.

This weighted average is taken now as the function of U to represent either the line intensity or the ionization probability, each on the arbitrary scale making it unity at $U=2$. To distinguish it from the uncorrected reduced intensity $j(U)$, of Table I, we shall call it the corrected reduced intensity, $j_0(U)$.

A graph of $j_0(U)$ is given in Fig. 4, with dotted curves for two empirical equations,

$$j_1(U)=2(m_1+2)\cdot(1-U^{-1})/(m_1+U) \quad (11)$$

and

$$j_2(U)=(2/U)^{m_2}(\log U/\log 2). \quad (12)$$

with $m_1=4$ and $m_2=0.783$.

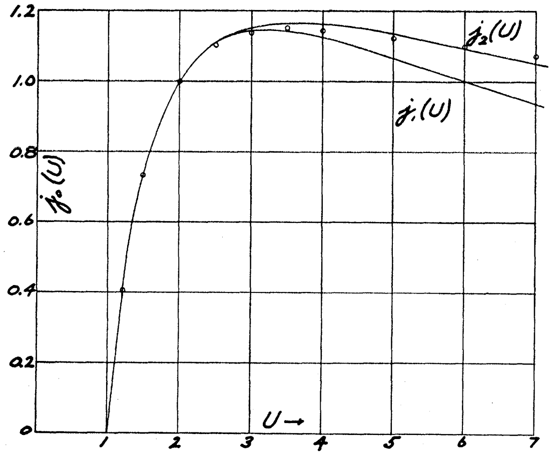

FIG. 4. Graph of corrected reduced intensity, $j_0(U)$ against U.

While $j_1(U)$ represented our 1928 data fairly well as far as they went with $m_1=3$, and it may be the more convenient function to use in some calculations, it is evidently not nearly so good as $j_2(U)$ for the whole range of U now available. In $j_2(U)$ the method of choice of a best value for m_2

TABLE VI. *Corrected reduced intensities,* $j_0(U)$.

	On Beryllium				*Free Silver Leaf, 1932–33*			
	1928		1932		On Cu holder	On Al holder		Weighted average
U	d, 170A	e, 280A	f, 450	i, 1400	k, 1900A	l, 1650	m, 1700	$j_0(U)$
1.2	0.403	0.404	0.406	[0.40]		[0.36]		0.404
1.5	0.748	0.726	0.737	(0.763)		(0.714)		0.733
2.5	1.115	1.103	1.100	1.095		1.105		1.103
3.0	(1.12)	(1.13)	1.150	1.129		1.140	1.137	1.138
3.5			1.162	1.135		1.153		1.153
4			1.145	1.134	1.148	1.149	1.146	1.145
5			(1.13)	(1.09)	1.131	1.128	1.130	1.123
6			(1.11)	(1.07)	1.115	1.101	1.085	1.099
7			[1.07]	[1.06]	1.095	1.062	1.070	1.072

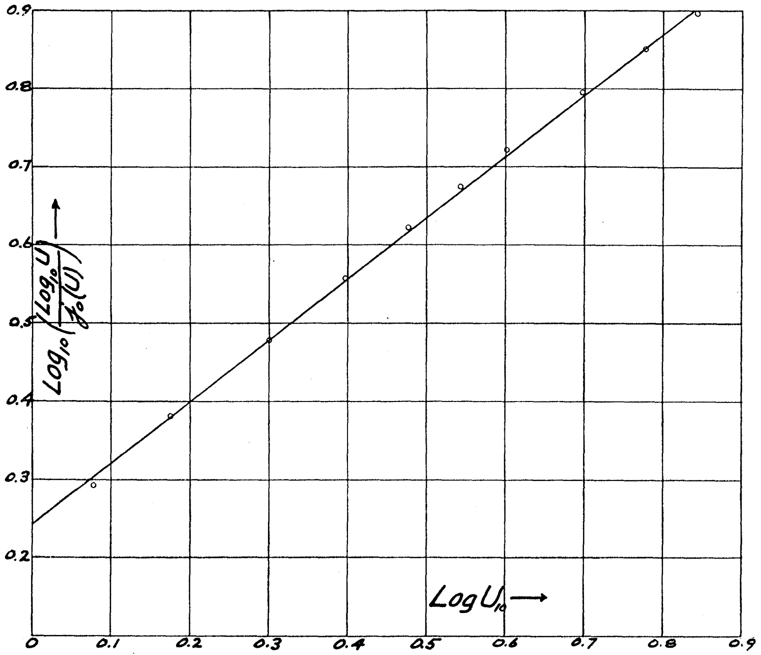

Fig. 5. The points show log $U/j_0(U)$ as a function of U; the line represents log $U/j_2(U)$ with $m_2=0.783$.

appears more clearly in Fig. 5, where the variables are chosen to make $j_2(U)$ give a straight line of slope m_2.

In addition to the data at the voltages tabulated here and shown in these graphs, we have data for film *e* at many other voltages. These were shown in a graph in our 1928 paper, but are not repeated here nor extended in that form, because they showed no departures beyond limits of error from a smooth curve, and there is every reason to expect the curve to be smooth, except at $U=1$.

The break at this point, however, is very significant, as noted in Section IA. It was therefore checked further with several films, and studied especially carefully with film *e*, with results shown in Fig. 6. Comparing this with the theoretical form for such a curve, shown in Fig. 3 above, it is evident that with a film so thin as this one, the whole region of upward curvature due to thick target effects is very small. This facilitates greatly the test for a finite slope at $U=1$, which consists, as noted above, in an extrapolation downward from a part of the curve safely above this thick-target region. Just how far one must go for this is difficult to say. The information on dU'/dx in Section IA would indicate 150 volts if the film were strictly uniform

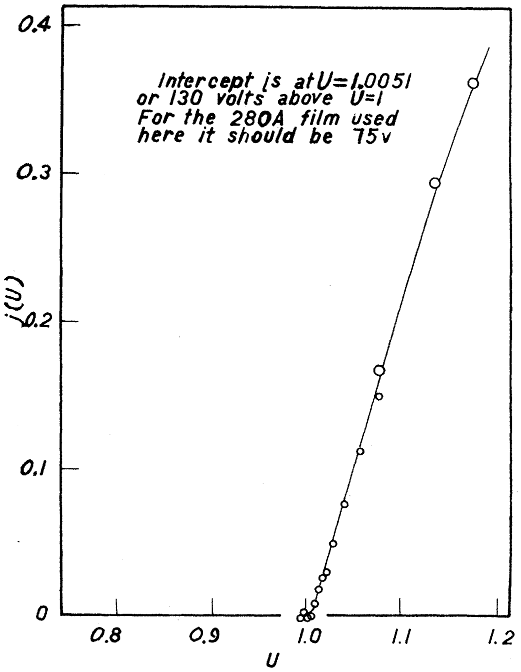

Fig. 6. Graph of $j(U)$ for film *e* near $U=1$.

and if it had no carbon on it. But strict uniformity is improbable, and there was enough carbon to retard cathode rays by an amount not negligible in comparison with 150 volts. At that, however, 150 volts takes us only to $U=1.006$, and one might begin the extrapolation many times as far above $U=1$ without impairing the test. It is evident that any such extrapolation proves the slope at $U=1$ to be finite and not zero.

Incidentally, the intercept of the extrapolated curve is about 130 volts above $U=1$, whereas the predicted value is 75 volts. The 55 volt difference is presumably the retardation in the carbon, and judging by our records of its color and our later measurements[6] on such films, this value is reasonable. With further study such measurements may prove useful as a means for measuring dU'/dx in films prepared for that purpose.

II. THEORETICAL

A. Comparison of wave mechanics with our experiments and others

The wave mechanics has been applied with considerable success to several other problems of electron impact, but relatively little has been done with it for the present problem. Elastic impacts and excitations of discrete levels have been treated by several authors, notably Massey and Mohr.[19] Ionization by electron impact has also received considerable attention from Ochiai,[20] Bethe[21] and others, even including work on the effects of relativity by a method due to Møller.[22] But so far as we have found, all the work on ionization has been done by Born's approximation, which is intended only for cathode rays of kinetic energy large compared to the ionization energy. Just how large it must be is uncertain, but one may question whether any such theory can be tested reliably with data extending only to $U=7$. This is even more questionable when, as in the present case, the data are not absolute probabilities, but only relative, because then the data even at $U=7$ acquire meaning only by comparison with data at still lower voltages.

With this understanding, however, we shall compare our data as well as we can with Bethe's[21] theory, which seems nearest to our conditions. This theory, like most, predicts an absolute probability of ionization by a cathode ray, rather than either our relative probability $j_0(U)$ or even the x-ray line intensity, which depends also on events subsequent to ionization. The absolute probability is defined most conveniently, not in terms of a path length Δx in metal, but as (probability of ionization) ÷ (number of atoms per unit area of target). This identifies it as the cross-section area of each atom effective for ionization. As applied to the present case of K electrons, by neglecting relativity, Bethe's value for this may be written as

$$\Phi_B(U)=(\pi e^2/V_K{}^2)\cdot(2b/U)\ln(4U/B), \quad (13)$$

where b and B are constants for any given element and shell, and the 2 comes from the number of electrons in the shell to be ionized.

Values are given for b for typical elements, including hydrogen and beryllium, for which it is 1, and silver, 0.32. B is described, for elements in which the K shell is well buried, as of the order of magnitude of unity. For hydrogen it becomes 0.638 for a cross section for ionization and excitation put together, but only 0.048 for ionization alone; and for valence electrons in general the corresponding constant is probably more of the order of 0.1 than 1. Beyond these qualitative statements, however, there is no value predicted for B.

To get what information is available about it, before comparing the theory with our data, one should examine such data as are available on thin targets at voltages so high that the approximations of the theory are justified. The best data of this sort are on gases, in which the data are obtainable directly from ionization measurements, rather than x-ray intensities. Helium is the best, being the only gas but hydrogen with only one shell to ionize, and fortunately this is a K shell. For helium, data have been taken by Hughes and Klein[23] Compton and Van Voorhis,[24]

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[19] H. S. W. Massey, Proc. Roy. Soc. **A129**, 616 (1930); H. S. W. Massey and C. B. O. Mohr, ibid. **135**, 258 and **136**, 289 (1932), and **139**, 187 (1933).

[20] K. Ochiai, Proc. Phys. Math. Soc. Japan **11**, 43 (1929).

[21] H. Bethe, Ann. d. Physik **5**, 325 (1930).

[22] C. Møller, Zeits. f. Physik **70**, 786 (1931); Ann. d. Physik **14**, 531 (1932).

[23] A. L. Hughes and E. Klein, Phys. Rev. **23**, 450 (1924).

[24] K. T. Compton and C. C. Van Voorhis, Phys. Rev. **26**, 436 (1925) and **27**, 724 (1926).

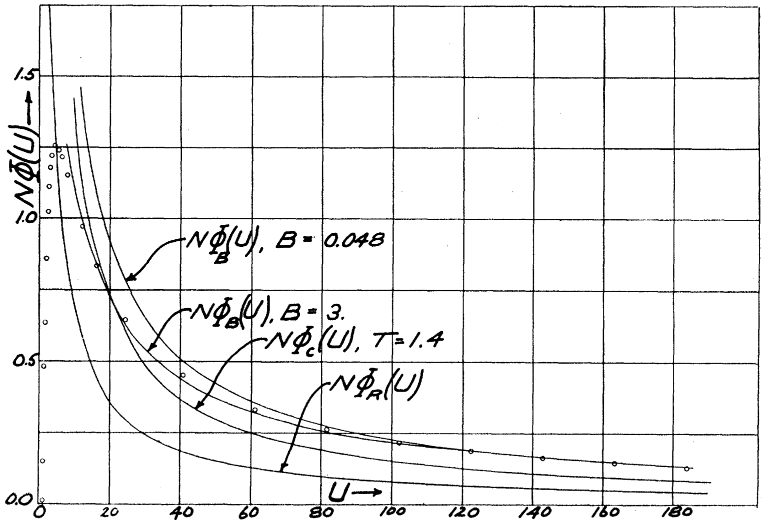

FIG. 7. Comparisons of Bethe's theory and others with Smith's data on helium. The functions $\Phi_R(U)$ and $\Phi_C(U)$ are explained in the next section.

and Smith.[25] They differ somewhat in detail but their graphs are all of the same general character as ours for silver, so far as our graph goes. Smith's data, the most recent, place the maximum at $U=$about 4.5, fairly near ours, though with a higher value of $j(U)$ there. His data extend to 4.5 kv or $U=183$. This is so high as to give the best evidence of all on the value of B. Furthermore his data are not merely comparisons of probabilities at different voltages, but absolute measurements. As such, they check b as well as B.

Multiplying $\Phi_B(U)$, with $b=1$ and $B=0.048$ (as for hydrogen), by the number of atoms per unit volume to which Smith reduced his data, the relation of this theory to helium is as shown in Fig. 7.

If these values of b and B are indeed the best, it would seem likely that Bethe's theory is accurate for values of U up in the hundreds, but that as U is reduced the theory becomes completely inapplicable long before reaching our upper limit $U=7$. Because of the approximations in the theory, however, it is possible that these values of b and B are not the best. We are therefore including also in Fig. 7 a graph for Bethe's theory with $b=1.75$ and $B=3$. These values were selected to fit the data as well as possible, by Professor W. V. Houston, to whom we wish to take this occasion to express our heartiest thanks for many very interesting conferences on this subject.

The fact that an increase of B from 0.048 to 3.0 makes it possible to fit the helium data so much farther down toward the low values of U will be recalled later in connection with our data, which are fitted best with $B=6$.

In the meantime, however, there are other data at high U's to be considered, taken by Lorenz[26] with aluminum. Lorenz used aluminum leaf, 8000A thick, and estimated the low-voltage limit for regarding this as a thin target at about 15 kv (about $U=10$) where the Thomson-Whiddington law would make the retardation only 1 kv. But this estimate does not allow for diffusion of the cathode rays. Bothe's diffusion formula, used in our calculations of the correction for diffusion in Section IC, gives the most probable deflection of a cathode ray under these conditions as 56°, making the increase in effective thickness 48 percent. Under such conditions, as noted with our Table II, the approximations used in the theory of the correction are very inaccurate, and the correction is probably greater than its calculated value. Practically, therefore, it seems difficult to interpret these data below about 25 or 30 kv, or $U=15$ to 20. From there up to Lorenz's limit, $U=33$, the

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[25] P. T. Smith, Phys. Rev. **36**, 1293 (1930).

[26] E. Lorenz, Zeits. f. Physik **51**, 71 (1928).

data can be corrected reasonably well by this formula. For this calculation, we have read the experimental values from his Fig. 8, and corrected them for diffusion, with results shown in our Fig. 8. Since the data are in an unknown unit, we have plotted the graph of Bethe's formula on arbitrary scales, chosen to fit the corrected intensity at 30 kv, both with $B=0$ and with $B=1$. Evidently the theory and the data would agree better if B could go below zero, but at least they are qualitatively alike, and zero is the best value for B here.

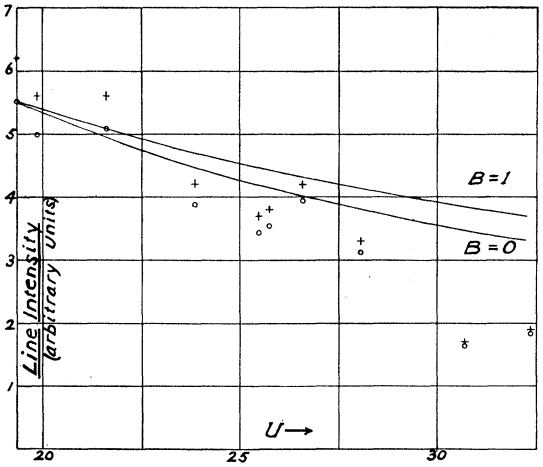

FIG. 8. Comparison of Lorenz's data on aluminum with Bethe's theory. Crosses, data as observed; circles, as corrected for diffusion.

Returning now to our own data, with the conflicting evidence on B reviewed above, we shall treat B as a purely arbitrary constant. Since our data, like Lorenz's, are in an unknown unit, we have used arbitrary scales for Bethe's probabilities, with $B=4$, 6 and 8, and plotted the results in Fig. 9. Remembering that the theory is not intended for voltages near $U=1$, there is no reason to expect the theoretical curve to strike the U axis there, and it is evident that the best value of B for our data is about 6.

High as this value of B is, it seems probable that others of the same sort may be found. Preliminary measurements here by Webster, Kirkpatrick and Pockman on the $L\alpha$ and β_1-lines of gold at $U=7$ to 14 indicate that the decline of intensities is very slow, much as one might expect from extrapolation of our data on silver. This suggests high values of B for the gold L_{22} and L_{21} electrons, respectively. The L_{11} electrons are not easy to test in gold because of the proximity of their strongest lines to those of the other sub-series. But Coster and van Zuylen[27] have used thin films of tungsten on beryllium, to compare the intensities of lines of the L sub-series. Up to $U=3.3$ for L_{11}, they find a rise in the ratio of the intensity of β_3 (of L_{11}) to β_1 (of L_{21}) or β_2 (of L_{22}), fast enough to indicate a considerable difference in the ionization probability functions. This suggests that the maximum of the function for L_{11} must occur at a higher value of U than those of L_{21} or L_{22}, and thus indicates a value of B for L_{11} even higher than for L_{21} or L_{22}.

(*Note added in proof:* It might be supposed that the slowness of this decline is due to the rise of L ionization produced indirectly, as a result of $K\alpha$ transitions. One line of evidence against this comes from the V_K^2 in the denominator of each of the theoretical ionization functions, because this predicts that the number of such indirect L ionizations is small. Other evidence is the absence of any noticeable breaks in graphs of the observed L intensities at the K ionization potential, which was included in the measurements, to test this point, even though it was excluded in the report made above, because of cathode-ray diffusion. The slowness of

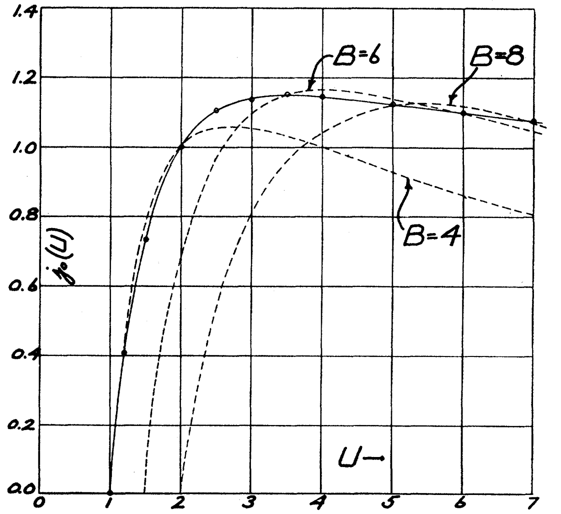

FIG. 9. Comparisons of Bethe's theory with our data on silver.

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[27] D. Coster and J. van Zuylen, Nature **129**, 942 (1932).

the decline of intensity therefore depends primarily on the direct L ionization, as assumed above in deducing the high values of B for the L electrons.)

It must be remembered, however, that any use of Bethe's equation for these low values of U is a severe strain on the approximations on which the theory is based. The use of his equation with large values of B, either in helium, silver, gold or tungsten, is therefore really on a semi-empirical basis. It is evident that the next step in testing the applicability of wave mechanics to the range covered by our data must be the development of a theory not limited to high values of U.

B. Nonrelativistic classical quantum theory

While the classical quantum theory is so badly out of date that we habitually discard it, the conclusion of the last section reminds us that the equations of classical theory are after all not bad as first approximations in many cases. In the present status of wave mechanics for this case, therefore, the classical theory should be tested as a temporary substitute.

Three theories of the classical type are at hand. The first, devised by Davis[28] in 1918, was based on the simplest model of an impact, namely the impact of hard elastic spheres. One of these was the cathode ray, the other something about the atom, not defined. Further hypotheses were equivalent to taking the mass of the atomic sphere as that of an electron and assuming that ionization would occur whenever classical mechanics indicated a transfer of energy as great as the ionization energy, but never otherwise. This theory predicted a value for $\Phi_0(U)$ given by

$$\Phi_D(U)=D(1-U^{-1}), \tag{14}$$

where D is an arbitrary constant.

The next theory, developed for ionization of gases by Thomson, and applied to x-rays by Rosseland,[29] was exactly like Davis's except that the spheres were electrons with the classical inverse-square repulsion. He predicted

$$\Phi_R(U)=(\pi e^2/V^2{}_K)\cdot 2\cdot(1-U^{-1})/U, \tag{15}$$

where the constant factors are the same as in Bethe's theory with $b=1$. Its relation to Bethe's theory and Smith's data is shown in Fig. 7.

Thomas[30] introduced two innovations into Rosseland's theory: (1) that the atomic electron, which had been treated as at rest, is in motion, with the speed of Bohr's K electron; (2) that the cathode ray, just before its encounter with the K electron, has a speed greater than it had before entering the atom, because it has been attracted by the nucleus. The result was

$$\Phi_T(U)=\frac{\pi e^2}{V^2{}_K}\cdot 2\cdot\frac{1-U^{-1}+(2T/3)(1-U^{-2})}{1+T+U}, \tag{16}$$

where T is the ratio of the orbital kinetic energy to the ionization energy, which for silver is 1.278.

To express the classical theory still more completely, we have recently[31] introduced another innovation, discussed in more detail in the next section of this paper. This is the deflection of a cathode ray by nuclear attraction within an atom, before it reaches the K electron it is to ionize. Since the K electrons are very near the nucleus and this deflection is always toward it, the effect must be an increase in the chance a cathode ray has of coming near a K electron. The change in the ionization probability is by a factor $(1+T+U)/U$. Thomas's calculations take account of all other important factors, so far as we can see, with no seriously inaccurate approximations except the neglect of relativity. Therefore we believe the application of this factor to his value for the ionization probability must give a reasonably complete and logical expression of the prediction of nonrelativistic classical quantum theory. With the subscript C for classical this gives

$$\Phi_C(U)=\frac{\pi e^2}{V^2{}_K}\cdot 2\cdot\frac{1-U^{-1}+(2T/3)(1-U^{-2})}{U}. \tag{17}$$

This formula, like Rosseland's and Bethe's, makes a prediction about the absolute value of the ionization probability. As Smith pointed out, and as Fig. 7 shows, the Thomson-Rosseland formula predicts ionization probabilities at high U's much too low to fit his data. The $(2T/3)$

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[28] B. Davis, Phys. Rev. **11**, 433 (1918).

[29] G. Rosseland, Phil. Mag. **45**, 65 (1923).

[30] L. H. Thomas, Proc. Camb. Phil. Soc. **23**, 829 (1927).

[31] D. L. Webster, W. W. Hansen and F. B. Duveneck, Phys. Rev. **43**, 384A (1933).

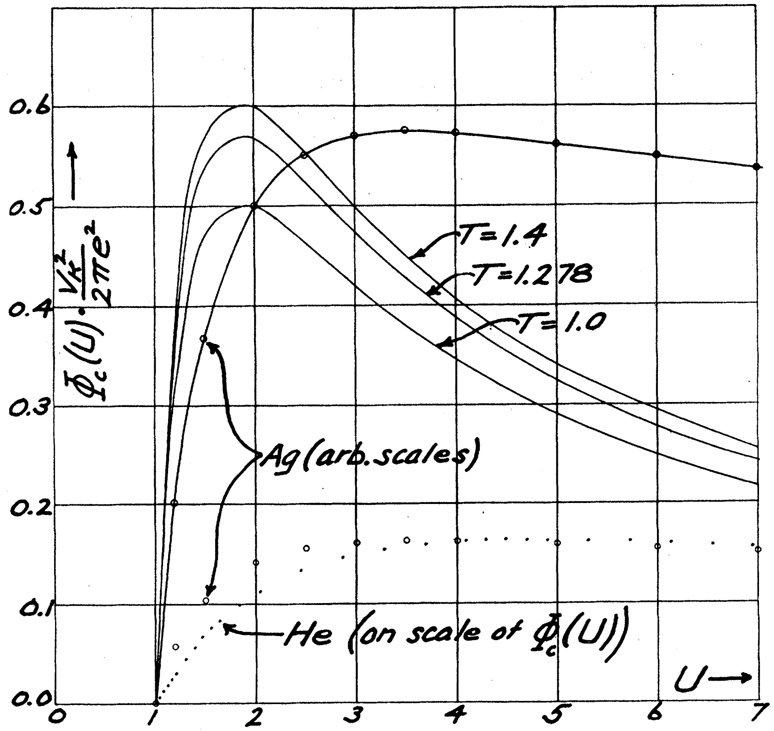

FIG. 10. Comparison of classical theory with data on silver and helium.

term introduced in this theory helps to reduce this discrepancy, as shown in Fig. 7. (*Note added in proof:* Here T is assumed to be 1.4, as given by strictly classical theory, though it might be better to use 1.6, as indicated by the observed ionization potentials.) At that, however, the theory is only an approximation, even at high voltages, not nearly so good as Bethe's.

To compare the classical theory with our data on silver, expressed in an unknown unit, $\Phi_C(U)$ must be in an arbitrary unit. Presumably this scale should be chosen to fit the curve to our data over as wide a range as possible. The fact is, however, it simply will not fit either silver or helium well on any scale, as shown in Fig. 10.

Turning to the data on other electrons discussed in Section IIA, which are also in unknown units, Lorenz's data on aluminum have about the same relation to this theory as to Bethe's with $B=0$, shown in Fig. 8. For L electrons, the classical theory for those with circular orbits is of course just like the theory for K electrons, and it would not fit our preliminary data on gold. For elliptical orbits (L_{11}) the only modification of the theory is that the constant T becomes an average around the orbit. This leaves it still practically unity, and gives no good way to account for the difference in the L ionization functions found by Coster and van Zuylen.

Evidently, even though the classical theory is a moderately good first approximation, though no more than that, for high values of U in helium, it is practically useless with $U<10$, even as a temporary substitute for a theory, for any element yet tested.

C. Theory of deflection of a cathode ray before an ionizing impact

It is indeed surprising that the classical quantum theory should depart from the data quite so badly as is shown by Fig. 10. Before accepting this conclusion, therefore, one may wish for more proof than our simple statement above, that the factor by which the probability of ionization is increased by the deflection of cathode rays really is $(1+T+U)/U$. The purpose of this section is therefore to give such a proof.

The essential basis for this proof is a feature of classical ionization theory pointed out by Thomas: for a cathode ray to transfer to a K electron enough energy for ionization, it must approach the K electron to a distance so small compared to that of either of them from the nucleus that their relative motion is practically like that of two free electrons. More specifically, in an atom of atomic number Z, this distance must be of the order of $1/Z$ of the radius of the K orbit, which we shall call a. Ionizing collisions occur therefore only in a thin shell, with a mean radius a and a somewhat indefinite thickness of the order of a few times a/Z. With no irreparable loss of rigor, this thickness will be treated as if it were definite (calling it b), and the value of any function of the distance r from the nucleus will be taken for any point in this shell to be the same as at $r=a$.

If a K electron is considered as exposed to impacts of an atmosphere of cathode rays (very rarefied, of course), all of one speed, the probability that it will be ionized in a time dt is evidently proportional to the density of this atmosphere. The present problem is therefore to find the factor by which the density of cathode rays in the K shell just defined differs from their density outside the atom. Considering this problem now as if the density were great enough to speak of a group of many cathode rays found in that shell all at any one instant, the ratio of densities is the reciprocal of the ratio of the volume of the shell to the volume which this group of cathode rays must have occupied before they entered the atom. This may be found by treating their paths like stream lines of a fluid, with a typical tube of flow as shown in Fig. 11. This tube may be described in spherical coordinates r, θ, ϕ, with the polar axis $\theta=0$ pointing at the cathode; and its cross section on a plane perpendicular to this axis, outside the atom, will be given in a plane polar coordinate system R, ϕ as $Rd\phi dR$. Considering the electrons in this stream that are found at any one instant crossing the K shell as defined above, their length along the stream there is $b \sec i$, where i is their angle of incidence on that shell. Outside the atom, therefore, the group must have had a length

$$B=(v_0/v_1)b \sec i, \tag{18}$$

where v_0 is their speed out there and v_1 their speed at the K shell. Although v_1 is the same for all such tubes of flow, i is not. B evidently increases with R, becoming infinite at $R=A$, the value of R for a path tangent to the K sphere. The volume to be calculated is therefore that of a sort of concave lens, of radius A and thickness B.

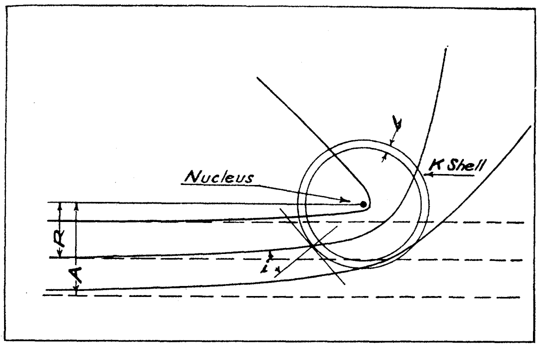

FIG. 11. Cathode-ray paths approaching a K shell.

Calling the densities outside the atom and in the K shall n_0 and n_1, respectively, and counting in n_1 the outgoing cathode rays as well as the incoming ones, it follows that

$$\tfrac{1}{2}n_1 \cdot 4\pi a^2 b = n_0 \int_0^A 2\pi R B dR. \tag{19}$$

If the electrostatic screening in the atom were too strongly concentrated near certain radii, this analysis might break down because it would be impossible to find a path from infinity tangent to the K shell. In any real atom, however, this does not happen, and it is easy to prove without any more specific assumptions about the field, that

$$n_1/n_0 = A/a = v_1/v_0 = [(1+T+U)/U]^{\frac{1}{2}}. \tag{20}$$

A part of this change of density, however, is due to the change of speed, which would make (n_1/n_0) exactly the reciprocal of this value, if it acted alone without the deflection. This is one of the effects included by Thomas in his calculation of $\Phi_T(U)$, and here it is combined with the deflection effect. To avoid correcting for it twice, therefore, we must divide it out before multiplying by the ratio of Eq. (20). In other words, $\Phi_T(U)$ must first be divided by (v_0/v_1) and then multiplied by (v_1/v_0). Altogether,

$$\Phi_C(U) = \Phi_T(U)\left(\frac{v_1}{v_0}\right)^2 = \Phi_T(U)\frac{1+T+U}{U}, \tag{21}$$

this last fraction being the point to be proved.

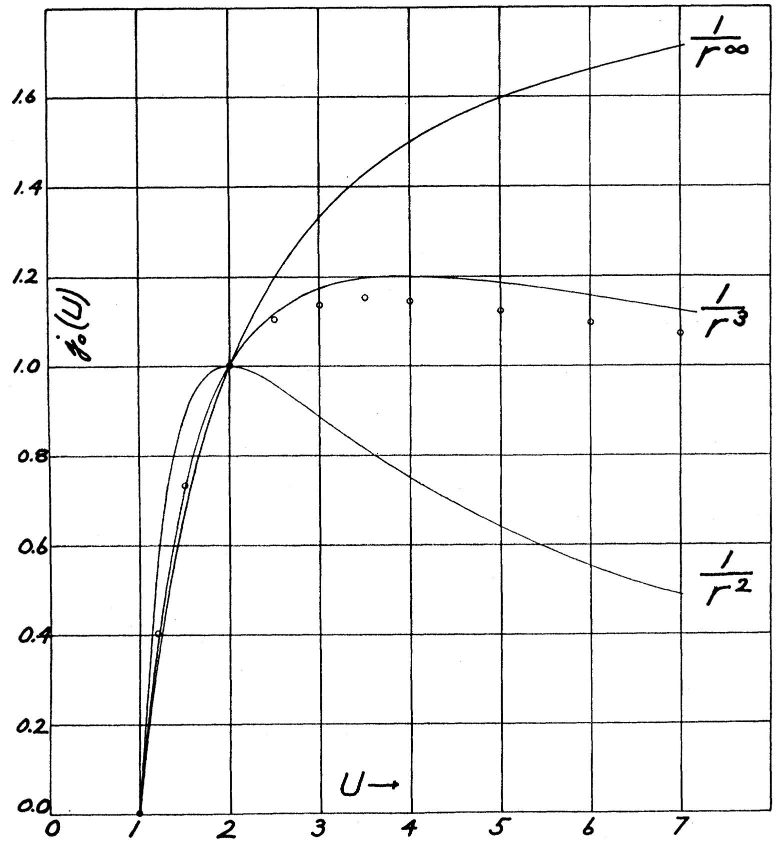

FIG. 12. Comparison of simple inverse-power theories with experiment: $j_R(U)$, inverse-square; $j_3(U)$, inverse-cube; $j_D(U)$ Davis's inverse infinity-power.

D. Modifications of classical quantum theory

Returning to the conclusion of Section IIB, that the nonrelativistic classical quantum theory was practically useless for silver K ionization even as a temporary approximation, and on the other hand remembering that nonrelativistic wave mechanics is very similar to classical theory in the well tested impacts of alpha-ray scattering, one may well question whether the change from classical theory to wave mechanics, without relativity, is likely to give a much better approximation. Then there is the question, how much difference relativity is likely to make. In classical orbit theory, as is well known, the effect of relativity is in the same direction as the effect that would be produced by changing the law of force from the inverse-square to a slightly higher inverse power. Is that, then, the sort of change we need here?

For a preliminary survey on this question, the easiest case to try is an inverse-cube law. Since Rosseland's theory differs but little from the more complete classical theory in its prediction for $j_0(U)$, even though they differ considerably on the absolute probability $\Phi_0(U)$, a rough test can be made on Rosseland's basis. With all assumptions exactly like his except on the force between the cathode ray and the K electron, the inverse-cube law there gives

$$j_3(U)=6/U\{(\pi/2\cos^{-1} U^{-\frac{1}{2}})^2-1\}. \quad (22)$$

This equation is compared with our data in Fig. 12.

While we cannot take the agreement of $j_3(U)$ with our data too literally as evidence for any such fantastic law of force, it is of interest to note that the difference between this function and the inverse-square function $j_R(U)$ is in line with the evidence on low-voltage ionizations also. Among these we may recall the ionization of helium reviewed in Section IIA. In fact, as noted there, while the maximum probability for helium occurs at $U=4.5$, near ours for silver, the intensities around $U=2$ are relatively lower. In other words, the change from classical theory needed for helium is even greater than for silver. Furthermore, even with silver, using voltages up to 180 kv, it is asking a good deal of relativity to change the effective law of force as much as this; and in the corresponding range for helium, up to 180 volts, such large effects of relativity seem quite impossible. For helium, a more important point may be the fact that Thomas's condition as to distances, that enabled him to treat the electrons as free, does not hold with $Z=2$. The more complicated 3-body analysis needed for this case may give results quite different from $\Phi_C(U)$. In either silver or helium, however, the change required by experiment must be something more or less equivalent in its results to a change in the exponent of the force law from -2 to about -3.

E. Derivatives at $U=1$

There is one prediction on which all the classical theories agree. This is on the slope of the graph of $j_0(U)$ at $U=1$: regardless of changes in assumptions, either about laws of force between electrons, motions of K electrons, or attractions by nuclei, this slope must be finite and not zero. This prediction is verified by experiment, both for silver and for helium.

For double ionization, however, the classical theory fails even here. The basis for this statement is the theory of x-ray satellites developed from Rosseland's theory by Wentzel and Druyvesteyn.[32] According to this theory, if U is now defined by reference to the minimum energy for double ionization, rather than single, then when U is but little greater than 1, the probability of double ionization should not vary as $(U-1)$, but as $(U-1)^2$, giving a graph with a zero slope at $U=1$. Experiment, however, contradicts this prediction flatly: Bleakney,[33] working with helium, finds a finite slope at $U=1$ for the double ionization probability, much like Smith's for single ionization.

This fact seems especially significant, because of the reason for the $(U-1)^2$ prediction, which is that double ionization is regarded in this theory as a succession of two ionizing impacts by the same cathode ray during its passage through one atom. These two impacts are related only by the condition that the first impact must not deprive the cathode ray of so much energy as to preclude ionization at the second impact. Otherwise they are separate events, each with its own probability of occurrence. The resulting probability of double ionization is therefore a product of the two single-ionization probabilities. It is this idea, in slightly more rigorous mathematical form, that accounts for the prediction of the exponent 2 in $(U-1)^2$.

The verdict of experiment, therefore, seems to be that double ionization shall not be regarded as a succession of two events, but as a single event. It seems reasonable to assume that it would be regarded so in the wave mechanics. The defect of the classical mechanics here, as in many cases of interaction between electrons, is then that it is too specific: it contradicts the uncertainty principle. In the case of double ionization at least, therefore, it seems reasonable to expect great changes when the wave mechanics is applied to the problem. So perhaps we may hope for similar improvement in the theory of single ionization also, despite the lack of notable changes in the theory of the simpler two-body impacts.

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[32] G. Wentzel, Ann. d. Physik **66**, 437 (1921); M. J. Druyvesteyn, *Dissertation*, Universiteit te Groningen, 1928. The equations from which these statements are deduced are in this dissertation, pp. 18–19.

[33] W. Bleakney, Atlantic City Meeting, Phys. Rev. **43**, 378A (1933).