A Determination of h/e from the Short Wave-Length Limit of the Continuous X-Ray Spectrum

JESSE DUMOND AND VERNON BOLLMAN California Institute of Technology and Occidental College (Received November 30, 1936)

Two precision determinations of the short wave-length limits of the continuous x-ray spectrum have been made, one in the region of 10,000 volts, the other in the region of 20,000 volts by the method of isochromats under very steady applied voltage. The two crystal spectrometer was used as a monochromator. The $K\beta_2$ line of molybdenum and the $L\beta_1$ line of tungsten were used for setting the monochromator. The experimental technique is fully described. A thin window tube with a nickel target coated with tungsten by evaporation was used as the x-ray source. The effect of the finite resolution of the two crystal spectrometer, its behavior as a function of wave-length, and the pitfalls resulting from the "tails" of the spectral window as defined by the selective bicrystalline reflection are carefully considered. The advantage of using a thin layer target of high atomic number on a back support of lower atomic number in order to minimize the danger from these pitfalls is explained. Arguments for the applicability of a correction to the measured voltage for the work function of the cathode are presented. All effects such as the finite resolution of the spectrometer tending to render the voltage threshold for a given wave-length setting less well defined are here called for brevity "smearing effects" and five different new methods of "desmearing" the isochromats or of locating the thresholds are considered.

I. PRESENT IMPORTANCE OF THE PROBLEM

A S Birge¹ has recently and repeatedly pointed out there still exists a stubborn and baffling discrepancy between the results of different types of experiment in the determination of the important natural constants e and h. So much emphasis has been placed on the discrepancy between the directly measured values of eobtained on the one hand from x-ray measurements and on the other hand from the oil drop experiment that now when the oil drop value of eseems in the opinion of many competent workers about to be rendered concordant with the x-ray value by more recent redeterminations of the viscosity of air² it is well worth while to reemphasize the discrepancies in other quarters which are still as great a mystery as ever. The presence of a hitherto unsuspected knee in the isochromat within a few volts of the quantum limit is shown to render inapplicable the only method so far in use for locating the threshold voltage, the "method of the projected tangent," which is also shown to contain other objectionable pitfalls. The experiment permits of determining either h/e or $e/h^{3/4}$ according to whether we assume the ruled grating wave-lengths of x-rays to be correct or make no such assumption but include the data from selective x-ray crystal reflection, crystal density, molecular weight and the Faraday constant as part of the computation. By these respective methods we obtain h/e = 1.3762 $\pm 0.0003 \times 10^{-17}$; $e/h^{3/4} = 2.0720 \pm 0.0004 \times 10^{10}$. These results agree with those of Kirkpatrick and Ross and those of Schaitberger on the same experiment with deviations which are small compared to the disagreement with two other entirely different experiments for determining functions of e and h. This discrepancy on the Birge-Bond diagram already emphasized by Birge is carefully discussed and possible causes for it are considered. Two possible objections to the present experiment are raised and we believe successfully disposed of. The practical impossibility of blaming this discrepancy on the short wave-length limit experiment is, we believe, convincingly proven by our results.

The diagram of Fig. 1 shows at a glance the present status of the problem. The reader is referred to the caption for an explanation of the diagram. We will not concern ourselves with the point marked "oil drop" since its proper position depends on the viscosity of air now in process of being redetermined. The discrepancy which we here wish to emphasize concerns the three points: I, the x-ray crystal value of e; II, the determination of $e/h^{3/5}$ from a combination of the measured values of the Rydberg constant and e/m; and, III, the determination of $e/h^{3/4}$ from the short wave-length limit of the continuous x-ray spectrum. These three points do not lie in the same straight line on the diagram. Any pair selected from the three experiments above yields values of *e* and *h* which are discordant with values obtained from any other pair by a much larger error than one would reasonably expect from internal consistency of the measurements and a

¹ Raymond Birge, Nature **137**, 187 (1936); Phys. Rev. **48**, 918 (1935). ² G. Kellström, Nature **136**, 682 (1935); Phys. Rev. **50**,

²G. Kellström, Nature 136, 682 (1955); Phys. Rev. 50 190 (1936).

careful consideration of all the sources of systematic error.

The order of accuracy attainable in measurements of e/m and R renders the point II by far the most accurate and reliable one of the three mentioned on the Birge-Bond diagram. It seems out of the question to expect any significant yielding here sufficient to explain even a small fraction of the discrepancy.

The authors have recently³ answered by an experimental test what they believe constituted the one remaining objection which it seemed possible to raise to the x-ray crystal method used in determining point I. The powdered calcite method discriminates definitely in favor of the x-ray crystal values of e as against values computed from points II and III, all three determinations by Bäcklin, Bearden and Söder-

³ DuMond and Bollman, Phys. Rev. 50, 524 (1936).

man lying inside the probable error of the first mentioned method. We attach no important significance to the slightly lower value obtained by the powder method which by its nature involves greater accidental errors and believe it safe now from these indications to assume the mean value of Bäcklin, Bearden, and Söderman as probably best, always conditional, of course, upon the correctness of the ruled grating values of x-ray wave-lengths.

As regards point III the experiment here described was performed in the hope that new light might be thrown on this discrepancy situation but it must be frankly admitted that the result has served simply to reemphasize the difficulty. The apparent impossibility of bringing point III into line with points I and II by any stretching of the short wave limit data will be made manifest in the following pages.



FIG. 1. The Birge-Bond diagram as applied by Birge to the problem of determining e. To each point on the diagram there correspond one or more experiments which determine in general some function of the constants e and h so that the results of each experiment or set of experiments can be written in the form $e = h^p \times$ (a measured constant). The Birge-Bond diagram above is plotted by assigning to h the arbitrary value h = 6.547, a value known to differ but little from the true one and computing nominal values of e from such equations. The nominal value of e called e_p is plotted as ordinate against the power p which represents the degree to which h was involved in its computation. Direct determinations of e which do not involve h at all thus appear at the extreme left. Since two unknowns e and h are involved, any three points may be consistent or inconsistent as to their evidence on the values of e and h. If three points are consistent, it is easily shown that they must lie in the same straight line and if otherwise, they are inconsistent. The experimental data leading to the establishment of points I, II and III are outlined in the last section near the end of this paper. If points lie in the same horizontal straight line, they indicate a value of h equal to that assumed in computing the diagram, h=6.547. Any two points determine a value of e which is given by the intercept on the y axis (at p=0) of a straight line through the points.

II. EXPERIMENTAL PROCEDURE

Our present experiment, like nearly all precision determinations of $e/h^{3/4}$ by observations on the short wave-length limit of the continuous x-ray spectrum, has been done by the method of isochromats. An x-ray spectrometer, in the present case a two-crystal ionization spectrometer, is set to select from the continuous spectrum a narrow band with its center coincident in wavelength with the center of a conveniently chosen standardizing line from the characteristic x-ray spectrum. Since the wave-lengths of these lines have been previously determined on the Siegbahn relative scale with high precision this part of the work need not be repeated. With the spectrometer thus set, an x-ray tube (not necessarily the one used to excite the standardizing line) is excited with gradually increasing applied voltage and the intensity of any of the radiation from it admitted through the spectrometer, the latter, being held always at the above constant setting, is measured in an ion chamber. As the quantum limit of the continuous spectrum from the tube pushes toward shorter wave-lengths with increasing voltage, a point is reached where continuous radiation finds its way through the bicrystalline selective reflection of the spectrometer and is registered as ionization in the ionization chamber. With increasing voltage the ionization then rises more or less suddenly as the short wave limit pushes forward to wave-lengths distinctly shorter than that for which the spectrometer is set. The threshold so defined fails to be abrupt principally because of the finite resolving power of the spectrometer.



FIG. 2. A typical spectral window curve.

The slit curve of the spectrometer

We shall make frequent reference to what we shall call the "slit curve" or the "spectral window curve" of the spectrometer. The mechanism of selective x-ray diffraction at the crystal surfaces combined with the imperfection of the crystal lattice itself define a region or "window" which the spectrometer selects from a continuous spectrum. This region or window cannot be made to have sharp abrupt edges or limits for its long and short wave-length boundaries by any experimental device of slits or screens because it is primarily the result of a diffraction phenomenon. This spectral window can thus be best described by plotting a curve such as the one shown in Fig. 2. A fair idea of the shape of such a curve can be obtained experimentally if the procedure for exploring the shape of a characteristic x-ray line be followed, choosing a line considerably narrower than the slit to be studied. The observed "line shape" is thus in reality chiefly descriptive of the "slit curve." Such a procedure is of course only approximate. The window curve is a characteristic of the spectrometer and should not be confused with an x-ray emission line. Characteristic of such window curves are the gradually diminishing asymptotic "tails," "wings," or "fillets" which mar the sharp definition of their short and long wave-length boundaries. No definite point of termination can be set for these "tails" and unfortunately for the experiment in question it is probable that they diminish at large distances from the maximum more or less as the inverse square of the distance. Thus even though the resolution of a spectrometer is excellent as regards the width of its slit curve at halfmaximum height there will always be a small amount of radiation admitted which may differ in wave-length by many times this half-maximum breadth from the central wave-length value. Furthermore if the continuous spectrum is such that at these remote wave-lengths the intensity is very considerably stronger than the intensity in the immediate neighborhood of the center of the slit curve it is evident that the intensity leaking through the tail of the slit may be very far from a negligible portion of the total and the center of gravity of the wave-lengths transmitted through the spectrometer may be quite different



FIG. 3. Diagram of constant potential d.c. supply and high voltage measuring circuits.

from what it would be if the continuous spectrum were nearly "flat."

Object of the experiment

The object of the experiment is to determine the critical or threshold voltage at which x-rays of a given wave-length λ just begin to appear as the shortest wave-lengths emitted in the continuous spectrum. The frequency ν corresponding to this wave-length is believed to be related to the threshold voltage V at which it just begins to be excited by the well-known relation

$$eV = h\nu \tag{1}$$

or what is equivalent

$$\lambda V/c = h/e. \tag{2}$$

Photoelectric experiment and the method of increments

Thus a single measurement of V and λ would appear to furnish sufficient data to compute h/e. In the closely related inverse experiment first performed by Millikan⁴ the critical stopping potential for photoelectrically emitted electrons is measured for a large number of incident wavelengths and the resulting curve of frequency or

⁴ R. A. Millikan, Phys. Rev. 1, 18 and 355 (1916).

wave number plotted against voltage turns out to be a straight line whose slope serves to compute h/e while the intercept of this line prolonged to the voltage axis gives in electron volts the "work function" of the photoelectrically emitting material. For brevity we shall call this the method of increments since it is a method of determining h/e from the increments of voltage and frequency $(V_1 - V_2)$ and $(\nu_1 - \nu_2)$ according to the equation

$$e(V_1 - V_2) = h(\nu_1 - \nu_2). \tag{3}$$

It is strange that in the x-ray experiment universally recognized as "the inverse photoelectric effect" the method of increments has never been applied at least according to any published report. The reason is probably to be found in the fact that while corrections for work function appear in the x-ray case just as surely as in the direct photoelectric effect these corrections are relatively so much smaller for the much higher voltages of the former than for the latter case that a resort to the method of voltage and frequency increments was not imperative. Nevertheless the present application of the method of increments has led us to some interesting conclusions.

The constant potential supply and high voltage measuring circuits

Ripple measurements.—Fig. 3 shows the diagram of electrical circuits used in this experiment. The 40 kw, 125 cycle alternator A is driven by a synchronous motor and is therefore very steady and free from fluctuations imposed by local variations in line voltage. Control of the high voltage applied to the x-ray tube is obtained by controlling the field of the alternator A supplied from batteries. A fine grained control of voltage was obtained by a small resistance paralleling a still lower fixed resistance in series with the current supplied to the transformer primary. This 125 cycle supply is stepped up and rectified by means of a valve tube rectified commercial set manufactured for medical use in deep therapy. The pulsating high potential output which is designed so that ground is midway between the potentials of the two terminals is filtered by two stages of condensers as shown with 125 henry inductances between stages. The filtering effect of this arrangement was greatly improved at very small extra expense by the addition of the two small 0.00075 microfarad condensers shunted around the inductances. These evidently need only have the dielectric strength sufficient to withstand safely the voltage drop across the inductance, that is to say, the ripple voltage prevailing at the first stage condensers. The capacity of 0.00075 microfarad is calculated to resonate with the inductance at 125 cycles or thereabouts. This tuning is, however, not very critical on account of the rather high resistance in the inductance.

So effective did this filter circuit prove to be that we found the ripple amplitude to ground to be less than 0.6 volt with the tube working at 10 milliamperes at which load it was operated. This ripple, as one would expect, was practically independent of the voltages of 20,000 or 10,000 volts used in the experiment. Without the 0.00075 mf condensers the ripple was three times as large.

The ripple amplitude was measured under operating conditions both near the tube and near the supply set (which are separated by two or three meters of transmission line) and found to be the same at both points. The ripple measurements were very easily made by means of an RCA cathode-ray oscilloscope C protected from



FIG. 4. Bridge for measuring megohm unit resistors.

the high voltage d.c. by a blocking condenser B made of two photographic plates from which the emulsion had been removed and which had been coated with thin sheet copper. The oscilloscope deflections obtained in series with this blocking condenser were calibrated by first applying by means of a resistance network a known small 125 cycle a.c. voltage to the oscilloscope with the same blocking condenser in series. The ripple from anode to ground was found to be slightly larger than the ripple from cathode to ground and this is to be expected because of the increased load on the anode side caused by the current flowing back through the cooling water supply, a long zigzag of glass tubing through which inlet and outlet water flows from the tap to the target and back to the drain.

E. O. Lawrence has suggested the possibility of very high radiofrequency ripple generated in the x-ray tube itself which would not be observed with the cathode-ray oscilloscope. We are indebted to G. Potapenko who has made an exploration in the vicinity of our x-ray tube with a very sensitive aperiodic thermocouple detector easily capable of detecting a source of 0.001 watt power and any radio wave-length down to a couple of centimeters. With nothing between this detector and the cathode and anode elements of the x-ray tube save the thin glass wall of the tube and a 1/16 inch enclosing tube of Bakelite and with the antenna of the detector at a distance of about 10 cms only, not the slightest indication of radiofrequency ripple could be observed with the tube in normal operation. Thus if such a ripple be present its energy is less than one part in two hundred thousand of the principal energy of the cathode-ray stream.

The high voltage measurements.—The high voltage measurements which are of highest importance in this experiment were made by means of a



FIG. 5. Method of extending the range of the potentiometer to obtain the ratio of the megohm units to a 40,000 ohm unit.

pair of 14 megohm resistance columns consisting of Shallcross wire wound resistances each connected to ground through a 1000 ohm resistance unit of the same kind of wire. The potential drop across these two 1000 ohm units in series was measured with a Leeds & Northrup latest type K potentiometer recently returned from a check by the manufacturers. Careful comparisons of our standard cell were made against three other standard cells which have been kept in this laboratory under carefully controlled conditions as laboratory standards. A check of the three latter cells as well as our own against a fourth standard cell freshly received from the makers with a calibration from the National Bureau of Standards was also made.

Since there is very likely to be an appreciable current to ground on account of the above mentioned unbalanced load from the watercooling system it is very essential that the ratio of each 14 megohm stack to its 1000 ohm resistor be exactly the same. If this equality of ratio is accurately satisfied it is then only necessary to multiply the potentiometer reading by this common ratio to get the potential at the tube no matter how much ground current may be present, whereas if the two ratios were different it would be necessary to take two potentiometer readings, one across each 1000 ohm resistor and add the results. This would have been very awkward for in practice the potentiometer was used as a continuous indicator to maintain the supply voltage constant at each chosen value during the ionization readings.

Calibration of the resistor ratios.—The high resistances consist of two stacks or columns of approximately 14 megohms each built up of Shallcross Super Akra-ohm units of one megohm each. These units, each of which is noninductively wound in 12 separate coils in a porcelain form are furnished by the manufacturers accurate to 0.1 percent. This means that the deviation of each megohm unit from one megohm will be of the order of 1000 ohms or less. We decided that the simplest way to obtain *equality* of the ratios of the 14 megohm stacks to their 1000 ohm resistors in the case of the two stacks would be to make the 1000 ohm resistors as nearly equal as possible first, then measure each of the megohm units accurately and distribute the twenty-eight units between the two stacks in such a way that their slight measured accidental excesses or defects over or under a megohm would balance out in the two stacks so as to make the two 14 megohm stacks as nearly identical as possible.

Throughout the work two instruments were used, one a Leeds & Northrup No. 4725 open dial Wheatstone bridge, the other a Leeds & Northrup type K potentiometer. The bridge had just been returned from the factory where it had been carefully checked and reconditioned. Its standard resistances were good in international ohms to 0.02 percent while the ratios of its ratio coils were good to 0.01 percent. The potentiometer also had been through a factory check not long before. It had a precision of about one part in forty thousand.

Equalization of the 1000 ohm (nominal) resistances was done with the L & N Wheatstone bridge and checked by means of the potentiometer (comparing the P.D.'s across the two resistors while carrying the same current). Wire was unwound from them until they were equalized to one part in 40,000. Their resistances as measured by the bridge were 999.18 and 999.17 international ohms.

For measurements of the megohm units the bridge shown in Fig. 4 was set up. Two 40,000 ohm (nominal) Shallcross resistors (good to about 0.1 percent) were used. With the L & N bridge these measured 40,048 and 40,060 ohms (international) (ratio, 1.00030). By putting them in series and measuring the P.D. across each one with the L & N potentiometer this ratio was very satisfactorily checked at the value 1.00029. One of the megohm units (not used in forming the stacks) was selected as a standard of reference and called R_1 . The other megohm units were successively placed in the arm of the bridge marked R_x . The bridge was balanced by adjusting

the appropriate one of the two decade boxes to the nearest ohm and leaving the other one shorted out. From the reading of this decade box the excess or defect in the resistance of R_x as compared to R_1 could readily be computed. The final result after a judicious allocation of the megohm units so as to equalize the stacks gave the ratio of each stack to R_1 as follows:

Stack No. 1 $\Sigma R_s/R_1 = 14.00881$, Stack No. 2 $\Sigma R_s/R_1 = 14.00877$.

It was now necessary to measure the ratio of each stack to its 1000 ohm resistor. The most direct method (but not the best) was to measure the arbitrary standard megohm unit R_1 with the L & N Wheatstone bridge. This gave $R_1 = 999,115$; 998,800 Av. = 998,960 international ohms. The ratio of R_1 to the resistor having 40,060 ohms was measured by passing current through both in series under a total P.D. of 1.5 volts and measuring the P.D. across each of them with the L & N potentiometer. This gave a check as good as the Wheatstone bridge measurements warranted (3 parts in 10,000). The currents in both methods are so small that a very sensitive galvanometer is required. To surmount this difficulty the device illustrated in Fig. 5 was used consisting of a divided circuit in one branch of which is placed R_1 and the 40,060 ohm resistance while in the other branch are two resistances one of about 50,000 ohms the other of about 2000 ohms. The applied voltage V was first made 1.5 volts and the ratio of the P.D.'s across the 50,000 and 2000 ohm resistances was measured with the potentiometer. Call this ratio N. The applied voltage V was then raised to 30 volts and the ratio of the P.D.'s marked v_1 and v_2 in the



FIG. 6. Method of extending the range of the potentiometer for measuring the ratio of the fourteen megohm stack to the 1000 ohm units in a single step. The constancy of this ratio as a function of temperature was checked in this way.

diagram was measured with the potentiometer. It is easy to see that the ratio of R to the 40,060 ohm resistance can now be computed by the formula

$$R_1/40,060 = (N+1)(v_2/v_1) - 1$$

Finally, by the same identical method the ratio of the 1000 ohm resistors to the 40,060 ohm resistor was determined. As a sample of the satisfactory agreements obtained we give some of the results of these ratio determinations. Subscripts indicate Wheatstone bridge values of resistances (except for R_1).

$$\frac{R_{40,060}}{R_{999.18}} = 40.0777;$$

$$\frac{R_{40,060}}{R_{999.17} + R_{999.18}} = 20.0393; \quad 20.0396,$$

whence

$$\frac{R_{40,060}}{R_{999,18}} = \frac{R_{40,060}}{R_{999,17}} = 40.0785 \pm 0.0006.$$

Similarly three independent determinations with slightly different values of the intermediate resistance ratio N above mentioned gave

$$\frac{R_{1(\text{megohm})}}{R_{40,060}} = 24.9408, 24.9398, 24.9393,$$

whence $\frac{R_{1(\text{megohm})}}{R_{40,060}} = 24.9396 \pm 0.0006.$

We believe the ratios measured by means of the potentiometer are far more accurate than the ratios to be computed from the resistance values given by the Wheatstone bridge. In all cases the ratios computed by the bridge method checked the ratios as measured by the potentiometer to within the precision to be expected from the bridge (say 0.03 percent) but we believe the potentiometer ratios to be accurate to about one part in forty thousand. Many checks and cross checks which space does not permit us to describe also gave highly satisfactory agreement. From these results we conclude that the ratio of $R_1/R_{999.18}$ was

$$R_1/R_{1000} = 999.5418 \pm 0.039.$$



FIG. 7. Profiles of the α doublet of molybdenum K radiation before and after grinding the calcite reflecting surfaces.

Now multiplying this by the ratio of either 14 megohm stack to R_1 and adding unity we get the final ratio of the entire stack plus the thousand ohm resistor to the thousand ohm resistor, that is to say, the ratio by which the potentiometer readings in the hookup of Fig. 3 must be multiplied to give the actual high voltages applied to the resistance stacks. This was

$14,003.38 \pm 0.55.$

A check of this ratio in a single step measurement was made, good to about one part in 15,000, by extending the range of the potentiometer as before according to Fig. 6. The ratio of the 50,000 ohm resistor to the 350 ohm resistor was first measured with the potentiometer with 1.5 volts for V. Then the ratio of v_2 to v_1 was measured with 180 volts from B batteries applied across V. This afforded a very satisfactory check of the above measured ratio and also permitted us to check this ratio for both stacks as a function of their working temperature.

Resistance ratio as function of temperature. Elimination of thermal e.m.f.—The stacks were constructed by simply screwing the 14 megohm units together terminal to terminal in a chain with the thousand ohm resistors hanging at the bottom. The entire chain was hung in a glass tube large enough to permit ample air circulation. The two stacks were then connected to the high voltage d.c. generating plant of Fig. 3 and allowed to come up to this equilibrium temperature by long continued operation. They were then disconnected from the high voltage and the ratio was repeatedly measured at equal time intervals by the method of Fig. 6. To the precision of this method (1 part in 15,000) no change in ratio could be detected in one stack. The other stack showed a decided change however as the stack cooled off. By reversing the polarity of the Bbattery supplying the 180 volts it was easy to establish that this apparent change in resistance ratio was in fact due to a thermal e.m.f. at the junction where the lowest megohm coil connects



FIG. 8. Continuous spectrum from a thin target.

to the thousand ohm coil and where the potentiometer is connected. Since the voltages measured here are low a small thermal e.m.f. can readily vitiate the measurement considerably. This thermal e.m.f. was completely eliminated by resoldering the joints at this point with advance resistance wire at the tap. The final resistance ratio on both stacks showed no detectable change over the entire range of temperature from full load to no load and was independent of the polarity of the battery.

Study of the spectral window.—The two-crystal spectrometer, Hoffman electrometer and ionization chamber with internal grid for reducing background have been described in a previous paper.⁵ The $K\beta_2$ line of molybdenum and the $L\beta_1$ line of tungsten were chosen as the lines for setting the crystals of the spectrometer. With the molybdenum tube in position the entire Kspectrum of molybdenum was carefully explored. Fig. 7 shows a profile of the α_1 , α_2 doublet. As these are the strongest K emission lines they were used for the study of the profile of the spectral window. After a little preliminary work on the isochromats of the continuous radiation near the short wave-length limit we reluctantly decided that in order to obtain the requisite ionization for precise measurements in a reasonable time it would be necessary to grind the surfaces of our calcite crystals. The limitation imposed by the random fluctuations of the natural ionization (cosmic rays and local radiation) was the chief factor necessitating this. Fig. 7 shows the α line profiles before and after grinding. The much greater breadth of the profile after grinding is the best justification for interpreting that profile as a good approximation to the spectral window curve. The curve before grinding, even, must be

considerably broader than the natural emission line profile because it too is a composition of the spectral window curve of the cleaved crystal surfaces with the natural emission line breadth. The vitiation of the profile obtained after grinding by the structure of this same emission line used to explore it can therefore, we feel, be safely regarded as slight especially in the wings of the profile.

Variation of window width with wave-length setting.-These studies of the window profile made it apparent that on a frequency or voltage scale the width as defined by the same spectrometer with the same crystals is different for different wave-length or frequency settings. The reason for this is easily understood. With ground crystals most of the width of the spectral window defined by the bicrystalline selective reflection in the two crystal spectrometer is caused by the geometrical disturbance of the crystal surfaces. This disturbance can be characterized by a parameter $\Delta \theta$ describing say the width at halfmaximum of the distribution curve of crystal disorientation. Whatever wave-length setting for which the crystals may be mutually orientated $\Delta \theta$ remains a constant and since $\sin \theta$ is nearly proportional to θ we have practically as a result that $\Delta \lambda$ is nearly a constant for any value of λ . Now, however, we have upon differentiating the equation

$$\lambda \nu = c,$$

$$\Delta \lambda / \lambda = -\Delta \nu / \nu,$$

$$\Delta \nu = -(\nu^2 / c) \Delta \lambda$$

whence multiplying by h

$$\Delta V = -\left(\Delta \lambda / hc\right) V^2,\tag{4}$$

which means that with increasing voltage the



FIG. 9. Continuous spectrum from a thick target conceived as the summation of infinitesmal thin target contributions.

⁵ DuMond and Hoyt, Phys. Rev. 36, 1702 (1930).

width of the spectral window expressed in volts increases approximately as the *square* of the voltage.

We wish to state here that this behavior is a consequence of the use of ground crystals. If cleaved crystals or crystals that have been polished and etched according to the specifications worked out at Cornell⁶ had been used the width $\Delta\lambda$ of the spectral window would then vary proportional to λ so as to maintain $\Delta\lambda/\lambda$ a constant. In consequence $\Delta \nu / \nu$ and $\Delta V / V$ would be constant for all settings ν , λ , or V. (To prove that $\Delta\lambda/\lambda$ should be a constant for crystals approximating perfection requires an appeal to the Darwin-Ewald-Prins dynamical theory of diffraction by a "perfect" crystal lattice which would occupy unjustified space here since it does not apply to the case in point.) This would be a far more desirable state of affairs for then the threshold voltage uncertainty introduced by the finite resolving power of the crystals would always represent the same percent error at all voltages and one could feasibly extend the present experiment to much higher voltages. The authors project doing exactly this with equipment whose construction has just been completed which permits of the use of a 30 kw x-ray tube. The large power will permit the use of polished and etched or freshly cleaved crystals.

Returning to the state of affairs with the ground crystals used in this experiment it is evident that since ΔV is proportional to V^2 a smaller percentage accuracy in the determination of the threshold voltage will be permitted by the effect of finite resolving power at higher voltages. For this reason the region of 20,000 volts was practically as high as it seemed worth while to go and the region of 10,000 volts promised the best precision attainable with workable intensities.

The x-ray tube.—A nickel target tube was chosen for the excitation of the continuous x-ray spectrum whose short wave-length limit was to be measured. This choice was governed by the fact that this particular tube was provided with an extremely thin glass window blown in the shape of a reentrant hemisphere in a projecting side tube and sufficiently thin to permit the



FIG. 10. Illustrating reduction in slope of continuous spectral distribution to be expected for a target consisting of a thin layer of tungsten laid upon a nickel backing. The knee K_3 should occur on the isochromat at voltages exceeding the threshold voltage by the amount required for an electron to penetrate the tungsten layer. The two slopes at K_3 should be about in proportion to the atomic numbers of nickel and tungsten.

exit of Ni K characteristic radiation in considerable quantities in a previous experiment. The importance of the determinations around 10,000 volts where the limited resolution of the spectrometer introduces so much less uncertainty in the voltage threshold than at higher voltages made this thin window especially desirable. It is of course highly desirable to have a target of the highest atomic number possible because as was shown by H. Kulenkampff⁷ the slope of the isochromat plotted on a voltage scale is proportional to the atomic number of the target. In spite of the fact that the tube we used had a target of nickel when it was first assembled we have every reason to believe that the coating of tungsten deposited on the nickel surface by evaporation from the cathode filament was of sufficient thickness to give the continuous spectrum the slope and shape to be expected from tungsten over a voltage range extending back from the short wave-length limit several hundred volts. There are certain advantages to be gained by having a target such as this one which while it cannot be described as thin in the sense of percent retardation of the impinging cathode rays is nevertheless only a few hundred volts thick and is backed up with a supporting material of much lower atomic number. Let us recall the theory of the production of the continuous x-ray spectrum first in a "thin" target, then in a

⁶ K. V. Manning, Rev. Sci. Inst. 5, 316 (1934).

⁷ H. Kulenkampff, Ann. d. Physik **69**, 548 (1922).

"thick" one. For the case of a target so thin that the impinging cathode rays lose a negligible fraction of their initial voltage in penetrating it, both theory⁸ and experiment⁹ indicate that the frequency spectrum excited by a homogeneous beam of electrons of voltage V will be, save at very low frequencies, a level plateau ending abruptly in a precipice at the short wave-length limit as indicated in Fig. 8. (The slight rise in this plateau at the low frequency end need not concern us here since this radiation would be absorbed before emerging from the window in the tube.) If we think now of the thick target as being divided into many successive thin layers each of these layers will emit a spectrum like that of Fig. 8 but only the first layer will be bombarded with cathode rays of the initial voltage. Successively deeper layers will receive electrons which have been retarded by passage through more and more layers above. Thus the triangular frequency spectrum from a thick target can be thought of as made up of infinitesimal contributions from these thin layers consisting of level plateaus with precipices at successively lower and lower frequencies as shown in Fig. 9. This rough first approximation to the mechanism of the production of the continuous spectrum in a thick target leaves out of account the effect of straggling of the electrons both in direction and speed and the effect of reemergence of some of the electrons from the target, but it seems clear that if a layer of tungsten sufficient to retard the impinging cathode rays by several hundred volts were present on top of the nickel target face then the continuous spectral distribution of x-ray intensity in the region from the quantum limit back a corresponding distance of several hundred volts would be characteristic of tungsten while the remainder of the spectrum would be characteristic of nickel bombarded by electrons retarded by the tungsten as indicated in Fig. 10.

The reduction in the intensity of the continuous spectrum in its longer wave-length regions starting at wave-lengths a few hundred "equivalent" volts back from the quantum limit caused by the low atomic number of the

nickel support seems to us to be a highly desirable effect for the following reason. The spectral "window" defined by the diffraction patterns of the crystals in the two crystal spectrometer has as we have already stated no sharp boundaries. The effect of the slight transparency of the tail of this window on its long wave-length side at remote distances from the "center" of the window is exaggerated if the continuous spectral intensity available to penetrate the tail of the window increases rapidly with increasing wave-length. Regions of the spectral window curve remote from its "center" by amounts equivalent to several hundred volts cannot be studied at all with present technique. It therefore seems most desirable to prevent the rapid increase of continuous spectral intensity with increasing wave-length after a point a few hundred volts beyond the quantum limit so as to minimize this effect for which we are not in a position to calculate a correction.

It may seem at first that the transparency of the spectral window several hundred volts away from its center could safely be neglected but this is not so certain. If, for instance, the transparency of the window decreased at large distances from its center according to the inverse square of the spectral distance (as both theory and experiment on the less remote parts of the "wings" indicate) while the spectral intensity increased linearly with this distance on the long wave-length side there would be no point beyond which one could safely neglect the transparency of the tail of the window because the total transmitted intensity would increase logarithmically with the position of this arbitrary point all the way down to zero wave-length. One would certainly hesitate to make a correction for the window transparency curve based on either theory or experiment over any such huge spectral range.

Estimates of the thickness of the tungsten coat on the target.—We believe the coat of deposited tungsten on our nickel target was more than "three hundred volts thick" for 20 kv cathode rays so that in Fig. 14 the knees K_1 and K_2 in the isochromat over the range observed by us cannot be attributed to the composite nature of the target. The four following lines of argument

⁸ A. Sommerfeld, Ann. d. Physik 11, 257 (1931).

⁹ W. W. Nicholas, National Bur. Stands. J. Research 2, 837 (1929).

support this belief and serve to place rough limits on the thickness of the tungsten film.

I. The nickel target showed strong emission of the tungsten L spectrum characteristic lines. In fact with about 20,000 volts applied to the tube these lines gave ionization in the chamber of the same or slightly greater intensity than those from a thick tungsten target tube which we had used for the wave-length setting. The nickel target tube, however, had the considerable advantage over the tungsten target tube of possessing a thin window which would make a very considerable difference for tungsten L radiation. We cannot, therefore, conclude that the tungsten layer was 20,000 volts thick especially when we recall what a large fraction of the characteristic line radiation from a target is indirectly excited by fluorescence. This evidence, however, does make it highly improbable that the tungsten layer was only a few atoms thick as it would necessarily be if the first knee K_2 in our isochromat were caused by it. We shall discuss this knee at greater length in its proper place.

II. The tube was originally built for the study of powder diffraction with Ni K radiation. Many long exposures had been made in this previous work with the tube totaling considerably more than 500 hours before it was used in the present experiment. With increase in the hours of life there seemed to be a noticeable decrease in the intensity of the nickel lines (though this might have been only a decrease in contrast) and a marked increase in the background of the powder diffraction patterns. This was what first led us to suspect the building up of a tungsten deposit on the target. The thickness of tungsten which will absorb half the intensity of the Ni $K\alpha_1$ line is 1.7×10⁻⁴ cm.

III. An x-ray tube filament run at ordinary emission temperatures usually has a life around 1000 hours and may lose by evaporation roughly 10 percent of its weight. From the weight of an entirely similar filament and the solid angle subtended by the target we compute that if all of the vaporized tungsten which hit the target during its operating life remained there it would have built up a layer 224A thick. Williams'¹⁰

formula for β -ray retardation gives for such a layer

 $d(\mathbf{kv})/dx = 1060 \rho \beta^{-1.4}$ or 455 volts retardation,

while the Thompson-Whiddington¹¹ formula which is probably better in this voltage range gives

$$V_0^2 - V_x^2 = 7.6 \times 10^{12} X$$
 or 836 volts retardation.

Estimating the first knee K_2 on our isochromat at 18 volts beyond the quantum limit the film of tungsten which would retard the cathode rays by this amount would be only about 9A thick. We therefore feel sure this knee is not ascribable to the composite nature of the target but is characteristic of the tungsten itself. In fact this knee, more or less pronounced, appears in previous work¹² with thick tungsten targets although it has heretofore been overlooked or interpreted as accidental, principally, we believe, because the limited resolving power of the spectrometer has more or less masked its presence.

IV. An effort was made to detect the effect of the $L_{\rm III}$ absorption discontinuity of tungsten in the continuous spectrum from the target. The height of the resulting discontinuity in the otherwise continuous spectrum if it could be measured would furnish information sufficient to compute the effective thickness of tungsten film traversed by the continuous radiation. This thickness would be given by the formula

$$x = (\log I_h/I_s)/(\mu_s - \mu_h).$$
 (5)

Here I_h and I_s are, respectively, the continuous spectrum intensities on the hard and soft sides of the discontinuity and μ_s and μ_h are the linear absorption coefficients on the soft and hard sides of the absorption edge. Or for such small absorption to good approximation

$$x = r/(\mu_s - \mu_h) \tag{6}$$

where r is the relative change in intensity $(I_h - I_s)/I_s$. Unfortunately there is an L emission line β_{10} of tungsten only two X.U. longer in wave-

¹⁰ E. J. Williams, Proc. Roy. Soc. London A130, 310 (1932).

¹¹ R. Whiddington, Proc. Roy. Soc. London A86, 360 (1912). ¹² Kirkpatrick and Ross, Phys. Rev. **45**, 457 (1934).



FIG. 11. Energy level diagram for electrons in an x-ray tube to illustrate the situation calling for a correction for the cathode work function. Hydraulic analog.

length than the position of the $L_{\rm III}$ absorption edge. This makes it necessary to extrapolate the continuous background from some considerable distance in order to ascertain whether a discontinuity is present and the discontinuity we were looking for was too small to measure with certainty for this reason although we believe it to have been just barely detected. A control in the form of a tungsten filter made of blotting paper impregnated with 2.21 mg/cm² of tungsten in the form of Na₂WO₄+2(H₂O) could easily be not only detected but roughly measured. We concluded from this that the effective thickness of the tungsten on our target was probably less than 0.95 mg/cm² or 5.4×10^{-5} cm.

We believe the use of a coating of heavy atomic number on top of a support of much lower atomic number to be a real improvement in the technique of this experiment for reasons already discussed, to which we shall return.

This tube was maintained at a very hard vacuum by a glass charcoal trap connected to it through a one inch glass tube. The charcoal and the entire tube had been thoroughly outgassed by long continued pumping in a bake oven and was then sealed off. The charcoal was kept cool in liquid air.

III. INTERPRETATION OF DATA

Corrections to the measured voltage

Only two small corrections to the measured voltage are necessary: The correction for the P.D. of the filament and the correction for the work function of the filament.

Referring to the diagram of Fig. 3 it is evident that the correction for the 6 volt filament P.D. requires that half of this operating P.D. across the filament, that is to say, three volts must be *added* to the voltage measured with the potentiometer. The electrons starting from the filament will be nearly uniformly distributed over a range of energies 6 volts wide and the corrected voltage will then refer to the middle of this range.

The correction for the work function of the filament merits some discussion as it seems to be regarded in certain quarters as of doubtful applicability. In Fig. 11, an energy level diagram of the energies assumed by electrons at different points in the x-ray tube, c represents the energy level of an electron just outside the cathode, T the energy level of an electron just outside the target while C' and T' are the energy levels of the electrons of (algebraically) highest energy

inside the cathode and target, respectively. These are the electrons of highest energy in the continuous Fermi degenerate gas distribution. The difference in level between C' and T' is the quantity measured in volts by the potentiometer in connection with the high resistances. The difference in level between C and T' is the maximum energy available for thermally emitted electrons in the production of x-rays and should therefore be the energy to be equated to $h\nu_{\rm max}$ or $(hc)/\lambda_{\rm min}$. These electrons can fall no lower than T' because there are no empty energy levels in the target below this. (The relative population of ionized levels in the target can easily be shown on energy considerations to be many orders of magnitude too small to furnish any observable x-ray intensity.) Not 1 percent of the electrons emitted at 2300°K can have an initial level higher than C by more than 0.9 volt as is well known from studies of thermionics. Thus it is evident that to the measured voltage must be added the difference in energy level between C and C'. This is the work function of the tungsten cathode or 4.52 volts. It is a fortunate fact that it is the cathode work function which must be considered in this correction because the hot cathode is thoroughly outgassed at its working temperature and its work function is very unlikely to be changed by surface impurity. The authors can see no reason for considering this a "doubtful" correction.13 The situation is simply that the electrons capable of transforming the greatest amount of energy into x-rays derive that energy from two sources; first, from the high tension d.c. generating equipment, second, from the electrically maintained thermal energy of the cathode. This work done on the electrons by the heat supplied to the cathode is well known and has been repeatedly measured directly¹⁴ by observing the enhanced cooling effect on the cathode when voltage is applied to a two element vacuum tube sufficient to give the thermionic emission current its saturation value as compared to the ordinary cathode cooling without electronic emission. In fact it furnishes one of the reliable methods of determining the thermionic work function.

To drive the argument home we have also shown in Fig. 11 an hydraulic analog of the situation requiring the correction for cathode work function. At C is the analog of the situation for a cold cathode while at H appears the analog for the hot cathode. Let us consider the cold cathode case first. Two vessels of water, one high above the other, are connected by a very fine narrow capillary tube in "series" with which is a water meter M calibrated so that its rate of flow reads directly the difference of "head" or level which is causing water to flow against. viscous resistance in the capillary. This is the analog to the two 14 megohm stacks and the potentiometer connected across the two thousand ohm shunt. This device evidently measures the difference in level between the free surfaces of the water in the two vessels. As shown, each of these free surfaces is at a certain distance below the top of the vessel containing the water. Now let us examine the hot cathode case. We suppose that some device supplies energy to agitate the water in the upper vessel so that a very little bit of it occasionally escapes over the edge in droplets. These droplets will fall in the lower vessel and will dissipate there an energy equal to the difference in head measured by the meter, M, plus the work done on a droplet by the agitating mechanism to lift the droplet over the edge of the vessel. The meter M will still obviously measure only the average difference in head which will be essentially unchanged by the agitation.

The two corrections which we have just outlined thus require that about 7.5 volts in all be added to the voltage measured by the potentiometer.

Smearing effects and the fillet

The authors have decided to adopt on trial the homely verb "to smear" to meet a situation arising frequently in physics. To smear shall mean to render less sharply defined or determined. A smearing effect may be caused by the unsharpness of the exploring tool and may or may not be irreparable. Thus if a spectrum is examined with a finite slit of known character or with a spectrometer whose spectral "window" has a determinable shape it may be possible to "desmear" the observed spectrum to some extent

¹³ But see Schaitberger's unsupported statement to the contrary. Schaitberger, Ann. d. Physik **24**, 84 (1935). ¹⁴ Davisson and Germer, Phys. Rev. **20**, 300 (1922); **24**,

¹⁴ Davisson and Germer, Phys. Rev. 20, 300 (1922) 666 (1924).



FIG. 12. Plot to rectangular coordinates of the threshold voltage (abscissae) against maximum emitted x-ray frequency (ordinates). At each "point" is shown a small view of the threshold region of the isochromat in its proper position on the voltage scale.

by the mathematical methods of integral equations and functionals. In this sense to "desmear" means to render more well defined or more homogeneous but not necessarily to completely purify observational data of every last vestige of inhomogeneity or indetermination.

A precise definition of the verb "to smear" is in order. We intend the verb to indicate an operation which in its simplest essential application may be thought of as acting on a single number or physical magnitude so as to transform it into a weighted complex of numbers. The weighted complex may be a continuous distribution or a discontinuous one. It may consist of an infinite set or a finite set of numbers. In what follows and more often than otherwise the single number is transformed into a continuous set of numbers grouped with symmetrical weighting around (above or below) the original number. The original number is then said to be smeared symmetrically. In order to definitely describe an operation of smearing it is obviously necessary to specify either by an analytic function or a plotted curve or a table of values or in some other way the characteristic distribution of weights to be attached to the set of numbers into which the original number is to be transformed. It is quite evident that this definition of smearing can be extended from that of an operation which acts on a single number to an operation which acts on a set of numbers, each number of the set suffering the same fate as all others and independently of them. It is a simple step from this to the concept of the smear of a smear. A word already common in mathematics closely related to smearing is

"composition." One speaks of the composition of two curves or functions by integration. We find, however, that this word in many cases is much easier to misunderstand.

The smearing effects in the present experiment are three, namely: 1. The finite resolving power of the spectrometer which is by far the most important. 2. The filament P.D. which is relatively unimportant. 3. The high voltage ripple which is completely negligible.

The actions of smearing effects may be regarded as operators and they frequently follow the commutative and distributive laws of ordinary algebra. Thus, as far as the result is concerned, it is entirely indifferent in what order or with what types of aggregation the three above mentioned effects are thought of as operating to produce the observed isochromat from what may be thought of as the "ideal" isochromat which would be observed if the three above effects could be rendered negligible.

The threshold voltage at which radiation just begins to appear of wave-lengths corresponding to the "center" of the spectral window of the spectrometer is smeared by the three effects just mentioned so as to give a "fillet" in place of a sharp inset point. It is the correct location of this inset point in spite of the masking fillet which constitutes one of the important problems in the present experiment.

Method of plotting the isochromats

The two threshold voltages which we have determined and their corresponding x-ray frequencies or wave numbers can be conceived as points lying on a curve expressing the functional relation between voltage and maximum emitted frequency in the x-ray tube, a curve which we expect to find a straight line passing through the origin when all the requisite voltage corrections have been made. The equation of this curve we expect to be $eV = h\nu$. We shall plot this curve with corrected voltage as the horizontal coordinate and with frequency as the vertical coordinate. For the purpose of computing e/h the absolute value of this frequency is important and may be determined either from the ruled grating wave-lengths of x-rays or from the internal data of this experiment itself taken in conjunction with computations based on the density and structure of crystals and the Faraday constant (in which case this experiment really determines $e/h^{3/4}$; but for our present purpose of representing the results it is merely important that the vertical coordinate shall be *proportional* to x-ray frequency or wave number. For the sake of definiteness we have plotted the vertical coordinate on a scale which represents the frequency (sec.⁻¹) computed from the ruled grating wavelengths of x-rays but we do not, of course, by so doing commit ourselves to the assumption that these are correct but only that they are proportional to the correct values. At the end of the paper we discuss the consequences of all possible assumptions and methods of computing both (e/h) based on the ruled grating x-ray wavelengths and $(e/h^{3/4})$ not so based.

Fig. 12 shows the normal way in which one might plot the above mentioned curve on rectangular coordinates. Since it is not really a point that we observe when we find the threshold voltage but rather a curve (the isochromat) in which the threshold point is somewhat masked by the fillet there is a real advantage in representing this curve with its fillet right in place on the voltage scale. Now to do this graphically in rectangular coordinates to a visible scale without sacrificing any of the precision of the voltage observations would require an impossibly large plot. We have therefore adopted the scheme of plotting in oblique coordinates. If one imagines the coordinate system of Fig. 12 subjected to a uniform shear so that the ν axis rotates about the origin O in a counterclockwise sense a new plot will be obtained like Fig. 13 in which the two isochromats in the neighborhood of the threshold points will be the one nearly vertically above the other while the zero points of their two voltage scales will be at very remote positions to the left far off the edge of the plot on an oblique straight line (the oblique ν axis) passing through the original O. This shearing of the plot can of course be endowed with *unlimited precision*. It is only necessary to plot the two voltage scales at vertical heights above the origin strictly proportional to the two x-ray frequencies at which the isochromats were observed and to locate these voltage scales horizontally in such a way that the voltages V_1' and V_2' which are situated exactly vertically over the origin strictly satisfy the



FIG. 13. Plot to oblique coordinates obtained by subjecting Fig. 12 to a uniform shear so as to bring the small views of the two isochromats into the same horizontal vicinity without sacrifice of scale.

relation $V_2'/V_1' = \nu_2/\nu_1$ with all the precision consistent with our knowledge of these quantities from the physical measurements that determine them. In this shearing distortion all lines that were originally straight remain straight and the graph of the equation $eV = h\nu$ is of course no exception. In the plot of our results, Fig. 14, we have shown a fan-shaped array of lines radiating from the origin whose inclinations correspond to those of graphs $eV = h\nu$ for various values of h/eon the assumption that the ruled grating values of x-ray wave-lengths are correct. The line for h/e=0 is obviously the skewed y axis and its very slight inclination to the horizontal indicates how very far to the left of the plot the zero points of the two voltage scales are.

Location of the threshold points

In the plot of Fig. 14 we have also shown to correct voltage scale a curve which we call the "g" curve and which is very nearly the spectral window curve of the spectrometer for the case of each isochromat. The vertical scale of these g curves is of course entirely arbitrary. Their horizontal position is also arbitrary. They are simply placed as shown for visual comparison with the fillet for which each is presumably responsible. The g curve is in fact a composite of the smearing effects of the spectral window curve and the 6 volt filament P.D. This latter influence changes the shape of the lower g curve in Fig. 14 slightly but makes no significant difference in the upper g curve. The 0.6 volt ripple has been therefore completely neglected. The composition of these two smearing effects is accomplished in the following way. Let w(x)



Fig. 14.

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FIG. 14. Our experimental results are here plotted as explained in Fig. 13. W_1 and W_2 are the points where the respective thresholds would have to be to make this experiment harmonize with points I and II of the Bond diagram. The finite resolution of the spectrometer, together with a slight contribution from filament P.D. are responsible for the "g" or "smearing" curves shown, which in turn satisfactorily explain the observed fillets on the isochromats. The widths of the g curves are to correct voltage scale but their positions on the voltage scale have no significance. At the left of this plot the level O corresponds to zero rate of drift of the electrometer which measures the ionization. The level L is proportional to the rate of drift with x-rays off while M is the rate of drift with x-rays on at voltages well below the threshold. L and M are indistinguishable on the lower voltage isochromat. The difference LM is principally diffuse scattering by the crystals of the spectrometer. The frequency for the upper isochromat should read 4.828×10^{18} /sec.

represent the spectral window curve expressed as a function of "equivalent voltage." Now we may assume with but little error that the filament emits over its six volt range as many electrons in one elementary voltage interval as in any other. Hence to get the curve g we smear the curve w by averaging it with uniformly distributed weight over a six volt range. The precise expression for this is

$$g(x) = \int_{-3}^{+3} w(x-z) du.$$
 (7)

These g curves may be thought of in their turn as smearing the ideal isochromat f by a similar mechanism to give the observed isochromat F(z); only in this case the range of smear has no sharp limits and the weighting over this range is not uniform but is distributed according to the ordinates of the g curve. The precise expression for this is

$$F(z) = \int_{-\infty}^{+\infty} g(x) f(x-z) dx.$$
 (8)

Eq. (8) is a little more general than necessary to express the situation in the present experiment and there are distinct advantages in an expression which takes into account the fact that the ideal isochromat (or what is the same thing with reversed sign of the independent variable, the continuous spectral distribution near the quantum limit) has a finite positive value everywhere on one side of the threshold point and vanishes completely everywhere on the other side.

In Fig. 15 let the independent variable x be thought of as proportional to x-ray frequency. g(x) is the window curve of the spectrometer (corrected for the slight smearing effect of filament P.D.). f(z-x) is the curve expressing the true distribution of the continuous x-ray spectrum as a function of frequency and voltage in the neighborhood of the limit. z is that value of x

where the curve f(z-x) meets the x axis and for all points to the right of which f vanishes. z is directly proportional to the voltage applied to the x-ray tube. The fact that f is here postulated as a function of (z-x) and not simply as f(z, x)gives explicit expression to the assumption that for small changes in the applied voltage the shape of the continuous x-ray spectrum in the vicinity of the quantum limit does not change appreciably. We are to think of the f(z-x) as a rigid foothill which simply slides uniformly to the right with increasing z. Now on the lower curve in Fig. 15 we plot the "isochromat" which is proportional at each point to the observed ionization produced by that portion of the spectrum f which can pass through the window g. This is

$$F(z) = \int_0^z g(x)f(z-x)dx.$$
 (9)

To get each ordinate of F such as the one shown we integrate over x the product of the two overlapping curves f and g up to x = z and plot the resulting value at the point z on the lower curve. Our problem is to find from the lower curve F(z), which is all we have given us, at what precise value P of z the threshold point of the curve f was in contact with some known essential feature of the curve g such for example as the abscissa value at its peak or its center of gravity. The particular feature of the g curve chosen to define the wavelength whose threshold voltage is sought is important. The authors believe that the peak abscissa or, what amounts to very nearly the same thing, an abscissa midway between two nearby values having equal ordinates on either side of the peak is preferable to the center of gravity because the wave-length of the former can be determined with less uncertainty than the wave-length of the center of gravity.

The only method of locating the threshold point used up to the present may be described as



FIG. 15. Illustrating how the isochromat is a composition of the continuous spectrum as it slides across the spectral window curve of the spectrometer. For any position z of the foot of the continuous spectrum on the frequency scale, x, the ordinate of the isochromat is the product integral of f and g from x=0 up to x=z.

the method of the projected tangent. The method consists in drawing a tangent to the isochromat at a point sufficiently remote from the fillet in the region of the quantum limit so that one feels that the isochromat has become and will remain for some distance sensibly a straight line. This tangent is then projected until it intersects the axis of abscissa (after subtracting off the residual ionization from cosmic rays and local radiation, etc., of course) and this point of intersection is taken as the threshold without explicit proof or analysis of what particular feature of the spectral window or g curve it refers to. We shall now proceed to prove that this method of the projected tangent gives the threshold point corresponding to the *center of gravity* of the g curve provided one can assume that for a sufficient distance back starting from the quantum limit the continuous x-ray spectral distribution is simply a sloping straight line. On this assumption Eq. (9) becomes

$$F(z) = \int_0^z S \cdot (z - x) \cdot g(x) dx, \qquad (10)$$

where S is simply a constant of proportionality, the slope of the curve f. Differentiating the integral with respect to z according to Leibniz' rule we have

$$F'(z) = \frac{d}{dz}F(z) = \int_0^z S \cdot g(x)dx + S \cdot (z-z) \cdot g(z),$$
(11)

the last term of which vanishes. Now, referring to Fig. 16, at some point z=b sufficiently far to the right, the short wave-length limit of the continuous spectrum may, as we here suppose, be considered to have crossed over the whole of the significant region of the spectral window curve gand on our assumption of linearity for the continuous spectrum the isochromat F(z) will remain a linearly increasing function indefinitely thereafter. To find the expression for the point Pgiven by the intersection of the projected tangent at b we have only to evaluate the quantity b-F(b)/F'(b)

$$F(b) = \int_0^b S \cdot (b - x)g(x)dx; \quad F'(b) = \int_0^b S \cdot g(x)dx;$$

$$b - F(b)/F'(b)$$

$$=b - \frac{S \cdot b \int_{0}^{b} g(x) dx}{S \int_{0}^{b} g(x) dx} + \frac{S \int_{0}^{b} x \cdot g(x) dx}{S \int_{0}^{b} g(x) dx}.$$
 (12)

The first two terms in the right-hand member cancel leaving as the expression for the value of zat P the last term which we see is simply the formula for the center of gravity of the g curve.

It is appropriate here to point out that even if the linear assumption with regard to the f curve were applicable this method of the projected tangent contains a dangerous pitfall closely associated with the nature of the wings of the gcurve. If these wings decrease in intensity no more rapidly than an inverse square law of distance from the center there will be no point bsufficiently far to the right to give a definite fixed position P. This is easily seen if we suppose the window curve given by the "witch" expression (with center at p)

$$g = [1 + (x - p)^2 / a^2]^{-1}.$$
 (13)

Then the expression for the center of gravity will be

$$\frac{\int_{0}^{b} \frac{x dx}{1 + (x - p)^{2} / a^{2}}}{\int_{0}^{b} \frac{dx}{1 + (x - p)^{2} / a^{2}}} = \frac{\frac{1}{2} a^{2} \log \left\{ \left[a^{2} + (b - p)^{2} \right] / \left[a^{2} + p^{2} \right] \right\} + \pi a p}{\pi a}.$$
(14)

With increase of b this expression obviously increases without limit. Physically this means that the curve F(z), Fig. 16 in spite of the assumed linear nature of f never becomes and remains sufficiently straight to fix a point b where one can safely draw a tangent but is always concave upward so that though this concavity decreases toward the right tangents drawn at points b farther and farther to the right continue always to intersect the axis at points P farther and farther to the right. Briefly the center of gravity of the "witch" type of curve (13) is indefinite in the sense that even if the limits of integration are infinitely remote the position of the center of gravity still depends on those limits.

The preceding method and its proof as we have stated is only applicable if there is a point b on the isochromat beyond which the effect of the wings of the g curve can be neglected and if from the quantum limit up to well beyond this point the distribution of the continuous x-ray spectrum can be assumed to be a sloping straight line. That this last is unfortunately not the case can be seen at a glance from our two observed isochromats in Fig. 14 which show beside the rather well-known upper knee K_1 a new knee K_2 , never before reported, much closer to the quantum limit. There is evidence for this second knee K_2 in the work of Kirkpatrick and Ross¹² (see their Fig. 2) but it was apparently treated by them as an accident of observation. We might easily have done the same thing had it not been for the evidence from the lower isochromat in the 10,000 volt region where the voltage resolution of the spectrometer is four times as good as at 20,000 volts. This is the first time to our knowledge that this experiment has ever been done at this voltage with the resolution available in the two crystal spectrometer.

The presence of the knee K_2 as well as the possible pitfall from the effect of the too slowly



FIG. 16. Illustrating the projected tangent method of locating the threshold point on the assumption that the f curve is linear.

decreasing wings of the g curve makes it imperative to find a better method of locating the threshold point than the method of the projected tangent.

Returning to Fig. 15 and expression (9) we see that it would be sufficient for our purposes to find the solution of the integral Eq. (9) where g and F are given and f is to be found. This is called by Whittaker the generalized equation of Abel's type. Ordinary methods recommended in the texts for reducing this to an equation of the "second kind" unfortunately break down with the type of g curve we have to deal with. It would be interesting of course to devise a general method for finding f over a large range of the independent variable and out of the five methods we have tried the first three listed below aimed at this. For our present purpose, however, it is not necessary to do this and the last two methods listed aimed only at locating the position of the threshold point which is all we need. A list of the five principal methods we have tried follows:

1. Solution of integral equation by solving a large number of simultaneous linear equations whose unknowns are successive ordinates of the f curve. This was abandoned after many attempts at approximate solutions. Solution depends too

much on the too uncertain properties of the remote wings of the g curve.

2. Solution of integral equation by assuming analytical expressions for g(x) and for f(z-x), in the case of the latter with adjustable parameters which are adjusted to make a least squares fit to the given F curve. This may be regarded as merely a device for reducing the number of equations of method 1. It is the standard method usually recommended for the practical solution of an integral equation whose functions are defined by physical observations. It suffers from the same weakness as the first method.

3. Solution of integral equation by a symbolic operator method of our own invention using the operator E of the difference calculus. We were able by this method to find a solving kernel in the form of a symbolic operator for certain simple types of g curve but were unable to generalize it to a g curve of the type given in this experiment.

4. To locate the threshold point on the higher voltage isochromat of Fig. 14 the lower voltage isochromat is assumed to be, relative thereto, a good approximation to the ideal isochromat (because it is four times as well resolved on a voltage scale). The fillet on this lower isochromat is removed for simplicity by the simple expedient of cutting it off along the projected tangent to the fillet at the lower side of the lower knee K_2 as shown by the oblique dotted line. The resulting curve is then smeared or composed with the g curve belonging to the upper isochromat and the resulting smeared curve now has a fillet beneath which there is a determined threshold point. This curve after multiplication by an appropriate normalizing factor and plotting on transparent paper can be superposed upon the upper isochromat and fitted thereto and this at once locates the position of the threshold point. Fig. 17 shows how convincing this fit is. The point marked 4 in Fig. 14 was located in this way. Minor objections may, of course, be raised to cutting off the lower fillet with a projected tangent from K_2 . It is difficult, however, to see how the ideal isochromat sought can help but fall somewhere between the two dotted lines from K_2 one of which is vertical, the other tangent to the fillet. There is nothing of an irregular nature in the wings of the g curve which could account for the knee K_2 and we feel confident that this knee must correspond to that voltage at which a similar break in the continuous x-ray spectral distribution close to its limit just passes over the peak of the g curve. Even if the continuous x-ray spectrum had a vertical precipice up to this first knee the threshold point could not be located at higher voltages than K_2 . Furthermore if the oblique dotted cut-off line is assumed correct and smeared or composed with the *lower* g curve a fillet is obtained which fits the lower isochromat very satisfactorily.

In Fig. 17 whether the curve PK_2K_1R or the curve QK_2K_1R is smeared with g makes a wholly indistinguishable difference in the resultant curve SL and we therefore locate the threshold 4 midway between P and Q and regard the range PQ as defining approximately the uncertainty of method 4.

This method just outlined is obviously based on the assumption that in passing from the 10,000 volt region of the lower curve to the 20,000 volt region of the upper curve the shape of the continuous x-ray spectrum in the immediate vicinity of the quantum limit does not change. This assumption is purely a guess and one which we feel is not too well supported by the facts since the knees of the artificially constructed isochromat *SL* do not fit the knees of the observed isochromat perfectly. We were therefore very happy to discover method 5 which we consider by far the best and most convincing.

5. This method of locating the threshold point consists simply in examining the first or second derivative curves obtained by plotting the *slope* of the isochromat (or the slope of its slope curve) as a function of voltage. These derivative curves contain pronounced peaks whose interpretation is quite clear on the basis of very simple and acceptable qualitative hypotheses about the general nature of the shape of the continuous x-ray distribution. These peaks serve to locate with a high degree of certainty and inner consistency the position of the threshold point. The most welcome and superior feature of this method is that the location of the threshold is the one corresponding to the *peak* of the g curve rather than to some dangerous conditionally convergent quantity like a center of gravity. Furthermore it is the one method which depends not at all on the shape of the wings of the g curve nor indeed to



FIG. 17. Showing the fit obtained in our method IV for locating the threshold. The observed isochromat is marked O while the curve marked SL was obtained by "smearing" the lower voltage isochromat with the g curve of higher voltage as explained in text.

any important extent on any property of the gcurve other than its feature of having a sharp peak. We have therefore great confidence in its reliability.

Fig. 18 illustrates the situation upon which method 5 depends. We have the choice of using either the first or second derivative methods. If the first derivative is used we assume as a sufficient approximation to the shape f of the continuous x-ray spectrum the curve having an abrupt vertical precipice at the quantum limit and a more or less pronounced break K_1 somewhat more remote from the limit. As stated in Eq. (9) we have

$$F(z) = \int_{0}^{z} f(z - x)g(x)dx.$$
 (15)

Differentiating this integral according to Leibniz' rule

$$\frac{dF(z)}{dz} = F'(z) = \int_0^z \left[\frac{\partial}{\partial z} f(z-x)\right] g(x) dx + f(0)g(z).$$
(16)

vertical precipice. There need be no fear of $[1+x^2/a^2]^{-1}$ we know that this integral will

trouble from this discontinuity since the function f in an analytic sense can be thought of as having the continuous dotted prolongation. The effect of a discontinuity is reproduced by the presence of zas the upper limit of the integral 15. This assures that *z* shall be that value of *x* where the quantum limit is, for any given voltage applied to produce the x-rays.

What does Eq. (16) tell us? It says that the first derivative of the isochromat can be decomposed into two additive terms one of which is a curve shaped exactly like the g curve and with its peak at the value of z corresponding to the value of xwhere the peak of the original g curve is indeed situated. It is only necessary for us to understand the general nature of the other term. If it were not for the knee K_1 the factor in square brackets in the integrand which represents the slope of the f curve would be a constant. The integral would then be

(a constant)
$$\int_0^z g(x) dx$$

Now f(0) is simply the height of the curve f at the and since g is not very different from a "witch"



FIG. 18. Illustrating the first and second derivative methods of locating the threshold.

closely resemble an antitangent curve, $\tan^{-1} z$, similar to the sketch Fig. 19 at A. The presence of the knee K_1 or any similar tendency for the slope of the f curve to decline with increase in its independent variable will distort the righthand part of the curve in Fig. 19 so as to produce a sag as at b. This will have little or no distorting effect, however, on the nearly straight region of this pseudo-antitangent curve near the point of inflection P. This is the region on which the peak of the term f(0)g(z) is superposed. Such a superposition, if the peak is at all pronounced and sharp, has very little effect on the location of the peak and even this small effect can be estimated and corrected for. The truth of this statement can be best appreciated by examining Fig. 20 in which the derivative curve of the 20,000 volt isochromat obtained by carefully taking tangent slopes has been plotted on the voltage scale. The two terms predicted in Eq. (16) are beautifully apparent and the sharpness of the peak contributed by the term $f(0) \cdot g(z)$ leaves little doubt as to the correct position of the threshold to within a very few volts. The partition of the derivative curve into the two terms of (16) involves admittedly a little artistic guesswork but it is easily seen that the peak of the g curve is such a pronounced feature that its location could be changed by only a very few volts at most even by the most extreme assumptions as to the shape of the two curves.

If now the second derivative is to be used for locating the threshold point we assume as a slightly better approximation to the shape f of the continuous x-ray spectrum the curve of Fig. 18 having a finite slope at the quantum limit and two knees K_2 and K_1 . On this assumption we can now strike out the second term of Eq. (16) since f(0) = 0 and differentiating again we obtain

$$\frac{d^2}{dz^2}F(z) = F''(z) = \int_0^z \left[\frac{\partial^2}{\partial z^2}f(z-x)\right]g(x)dx + \left[\frac{\partial}{\partial z}f(z-x)\right]_{x=z} \cdot g(z). \quad (17)$$

Here again we have two additive terms composing the second derivative curve one of which is simply g(z) with a coefficient proportional to the slope of the continuous spectrum at the quantum limit. It is simply necessary as before to inquire qualitatively what the other term, the integral, will resemble to be prepared to understand the result. The presence of the two more or less concentrated knees K_1 and K_2 correspond to finite sudden diminutions in slope with increase of the independent variable of f and give to the integral in 17 somewhat the nature of a Lebesgue integral, because the bracketed coefficient in the integrand may be regarded as assuming a value after the nature of a δ function (negative in sign) only at two concentrated points of (z-x) namely K_1 and K_2 . In consequence the integral terms of Eq. (17) will appear as two curves each shaped exactly like the principal g curve but with negative intensities and with displacements to the right of the principal g curve equal to the displacements in the continuous x-ray spectrum of K_2 and K_1 to the left of the quantum limit. The principal (positive) g curve and the two inverted g curves g_1 and g_2 just mentioned will



FIG. 19. General appearance of the contribution of the first term of the right-hand member of Eq. (16).



FIG. 20. Location of threshold of higher voltage isochromat with first derivative analysis. Note the contributions of the two terms of Eq. (16).

have relative intensities proportional respectively to the slope of the continuous spectrum at the quantum limit and to the two discrete changes in slope K_1 and K_2 . An examination of Fig. 21 shows how beautifully all of these predicted features are brought out in the second derivative curve. Here again the partition of the second derivative into g, g_1 and g_2 involves a little guesswork but the position of the peak of g is very clearly fixed in spite of this.

The use of these two derivative methods gives the two points marked 51 and 52 as threshold points in Fig. 14, the point 51 referring to the first derivative method. An average between these two points gives us the voltage 19,915 for the threshold on the upper isochromat. The voltage scales in Figs. 14, 17, 20 and 21 are our potentiometer observations multiplied by the resistance ratio already mentioned, 14,003, with the 7.5 volt correction for filament P.D. and cathode work function added thereto. To get the true value in international volts, however, this must be diminished by 0.015 percent, a correction shown to be required by a very careful recheck of the voltages of our standard cells against a new cell just calibrated at the National Bureau of Standards.

IV. CRITICAL DISCUSSION OF RESULT

Inescapability of the discrepancy on the Birge-Bond diagram

In Fig. 14 for comparison with the observed thresholds we have plotted points W_1 and W_2



FIG. 21. Location of threshold of higher voltage isochromat with second derivative analysis. The upright g curve contributed by the second term of the right hand member of Eq. (17) and the two displaced and inverted g curves from the first terms of that equation are clear cut. The black-ened peaks of the second derivative curve indicate approximately the uncertainty in the value of the second derivative at these points.

where the threshold would have to be in order to make the results of this experiment harmonize with the results of experiments I and II on the Birge-Bond diagram of Fig. 1. Clearly it is very difficult to believe that the thresholds can in reality be at W_1 and W_2 through some vagary of the smearing effect of the g curve. The presence of the knee K_2 would be very difficult to understand if W_1 and W_2 were the true thresholds. The value of h/e indicated by Fig. 14 is 1.3762×10^{-17} . This is the value computed if we assume the ruled grating wave-lengths of x-rays to be correct in absolute units (Mo $K\beta_2=0.6210 \times 10^{-8}$ cm, $WL\beta_1=1.2818 \times 10^{-8}$ cm).¹⁵ We may

¹⁵ On the Siegbahn scale of x-ray wave-lengths (in which d_1 for calcite = 3.02904) according to Larsson, Phil. Mag. 3, 1136 (1927) the wave-length of Mo $K\beta_2$ is 0.619698 while according to Friman, Zeits. f. Physik **39**, 813 (1926) the wave-length of WL β_1 is 1.27917. Both of these values are in

from this also compute $e/h^{3/4}$ independent of any such assumption as to the absolute value of x-ray wave-lengths. This yields the result $e/h^{3/4}$ = 2.0720×10¹⁰ in rather good agreement with the value obtained by Kirkpatrick and Ross. The slight disagreement is extremely small in comparison to the discrepancy between this experiment and experiments I and II of the Birge-Bond diagram. Our slight disagreement with Ross and Kirkpatrick is in part accounted for by the existence of the knee K_2 of which they were not aware but this is not sufficient to explain all of it and we do not know the cause of the remainder.

It is worth pointing out that if the discrepancy between the results of this experiment (III) and the results of experiments I and II on the Birge-Bond diagram is to be blamed on this experiment (III) our results would indicate that the photons of a given wave-length or frequency appear too soon that is at voltages applied to the x-ray tube *lower* than one would expect from conclusions based on I and II. This is much more difficult to understand than would be a discrepancy in the other direction. Two possible causes for such a shift of the threshold voltage to lower values have been suggested but we believe that strong evidence can be presented against these suggestions.

Attempts to account for the discrepancy from causes inherent in the present experiment

First suggestion.—It is suggested that the vigorous ejection by the primary cathode rays of secondary electrons from the target in the region of the focal spot perhaps maintains a positively charged very thin layer at this point which for some reason is not neutralized at a sufficiently rapid rate by electron flow in the metal target to prevent the building up of a considerably more positive potential locally than the potential of the target as a whole measured by the potentiometer. Those infrequent electron collisions which take place very close to the surface of the

target and result in the "hardest" x-rays emitted will have the advantage of the extra work done on the cathode rays by the field of this positive layer.

There are at least three objections to this hypothesis. One is that to explain the threshold shift in the case of our 20,000 volt isochromat it would require the positive layer to be about 70 volts more positive than the target. On the other hand it is very difficult to see how such a layer could be many atoms thick. This then would mean that between this layer and the metal target behind it there would exist electrical fields of staggering proportions-billions of volts per centimeter. It becomes terribly difficult to imagine any mechanism of metallic conductivity to explain how such fields are maintained. Furthermore any such explanation must also explain why when the tube is operated around 10,000 volts the threshold shift is only of the order of 30 or 35 volts instead of 70 in the case of 20,000 volt operation. Note that from Fig. 14 one is obliged to find an explanation in terms of a *shift* proportional to voltage. Further investigation is, of course, needed to establish with accuracy just how linear this proportionality is. Finally this explanation must contain some reason to explain why the threshold shift is independent of the cathode-ray current in the tube.

Second suggestion.—It is suggested that photoelectrons are ejected from the cathode and from its focusing cup both of which are subjected to intense x-rays from the target and that these have a preponderant initial energy of some 70 volts for the 20,000 volt x-rays and 35 volts for the 10,000 volt x-rays. These photoelectrons will strike the target then with the requisite excess of energy over the energy to be expected from ordinary thermally emitted electrons to explain the shift in the threshold.

If this were correct one would expect to see the slope of the isochromat increase with increasing voltage all the way up to (or perhaps abruptly at) the points W_1 and W_2 , Fig. 14, where one expects to see the spectrum from the ordinary thermally emitted electrons first appear. Instead the curve bends the other way. Work¹⁶ done on the velocity distribution of both primary and secondary electrons ejected by x-rays shows that

good accord with other observers. Bearden (see reference 20) has carefully reviewed the evidence from different sources and finds very convincingly that over a wide range of wave-lengths the ruled grating scale differs from his crystal scale (where $d_{\infty}=3.0281$, however) by the amount $(\lambda_{g}-\lambda_{c})/\lambda_{c}=0.248$ percent. Or reducing this to the Siegbahn scale above it is 0.2035 percent. In this way we get for the ruled grating values of the wave-lengths of Mo $K\beta_{2}$ and WL β_{1} 0.6210×10⁻⁸ cm, and 1.2818×10⁻⁸ cm, respectively.

¹⁶ L. Simons, Proc. Phys. Soc. London 37, 58 (1924).



FIG. 22. Showing target and cathode to scale in x-ray tube test for proportionate amount of excess energy electrons by photoelectric ejection. Connection of galvanometer is also shown.

the great bulk of such electrons are secondaries ejected by the fast photoelectrons and that these secondaries have a well marked peak in their velocity distribution curve at a velocity corresponding to about 3.5 volts, a velocity far too low to explain the required shift in the threshold point. Furthermore, strange as it may seem, the most copiously occurring voltage of these secondary electrons, 3.5 volts, is independent of the voltage of the x-rays indirectly responsible for them. Further work¹⁷ shows that for x-rays as far down in the scale as 270 volts ($K\alpha$ line of carbon) the bulk of the ejected electrons have much the same velocity distribution as those ejected by much harder x-rays of the order of those in this experiment. It thus becomes very hard to see how such an effect could give a shift of the threshold proportional to voltage. The strongest objection of all, however, is based on the intensity to be expected from such excess energy electrons. In the two references cited^{16, 17} the total emitted electron currents had to be measured by electrometer and electroscope methods and were probably of the order of 10^{-14} amperes at most. We have made a very rough computation based on energy considerations and the known efficiency of production of x-rays to place an upper limit on the ratio of the total number of such excess energy electrons that could be produced to the number of cathoderay electrons. This computation repeatedly gives the benefit of the doubt to the side of more rather than less of these electrons and is probably a very gross over estimate. The extreme upper limit fixed in this way for the excess energy

electrons of all kinds is 1 percent of the total cathode-ray current. Since this computation may, however, be in error for some reason we have felt it safer to measure in a rough experiment the order of magnitude of the photoelectron current to be expected. The 30 kilowatt (continuous rating) x-ray tube which forms a part of the Watters Memorial Laboratory equipment of this Institute is designed with the cathode filament enclosed in a shield consisting of a cylindrical steel box B from which both terminals of the cathode are insulated as shown in Fig. 22. This box is carried on the end of a steel tube Twhich completely encloses and shields the cathode leads. The cathode rays stream through the hole in the box and its flat steel end is bathed in the x-rays generated when these cathode rays strike the gold surfaced target distant from the flat front of the cathode box by only $1\frac{1}{4}''$ measured normally. It is evident from the scale drawing that the front of this box subtends a large solid angle at the focal spot. (It is in fact a much larger solid angle than that subtended by the steel focusing cup in the tube used in the main part of the experiment described in this paper.) Any photoelectrons ejected from this steel surface will be instantly transported to the target and the electron current thus leaving the box was measured by means of a galvanometer G connected as shown in Fig. 22. The connection through the galvanometer to the box was such as to make the box slightly more electronegative than the most negative emitting part of the hot filament. With 10 ma thermionic current and 20,000 volts very steady potential (reproducing the conditions of our main experi-

¹⁷ E. Radberg, Proc. Roy. Soc. 120, 385 (1928).

ment) the total electron current leaving the shield was 0.02 milliampere or only 0.2 percent of the thermionic current. However, a part of this must be regarded as a spurious effect since with only the filament operating but no high voltage and therefore no x-rays we could still get galvanometer deflections indicating electron currents leaving the shield of 0.007 milliampere. Furthermore with the high voltage of 20,000 volts applied but with the cathode cold so as to give no thermionic current the galvanometer still indicated an apparent 0.0035 milliampere of electron current flowing out of the shield probably the result of insulator leaks. Thus there seems no doubt that the photoelectrically ejected electrons of all velocities together constituted considerably less than 0.2 percent of the cathode rays striking the target.

One must think then of this excess energy class of electrons, even if it be homogeneous and of initial velocity 70 volts, as itself generating a continuous x-ray spectrum with a threshold at shorter wave-lengths but in its entirety only 0.2 percent (and probably less than this) as intense as the total continuous spectrum from the ordinary thermally emitted electrons whose threshold corresponds to some point like W_1 or W_2 of Fig. 14. It strains one's credulity to the breaking point to believe that a shift of the threshold of the isochromats shown in Fig. 14 could be explained by such a mechanism.

The discrepancy situation on the Birge-Bond diagram

We believe that from the discrepancy exemplified by points I, II and III on the Birge-Bond diagram arises a situation well worth reemphasizing and one which both experimental and theoretical physicists should take very seriously. The better to illustrate the serious nature of this situation we summarize below the formulae applying in each of the three experiments and the various measured quantities entering into the determination. Let us regard each experiment as a method of determining e as a function of measured values and the unknown, h, so that the result of any experiment could be written in the type form

 $e = h^p \cdot [$ function of measured constants].

For experiment I, p=0 for II p=3/5, for III

the present experiment, p=3/4 or unity depending on the assumptions made. Since the two unknowns e and h are involved two experiments are necessary in general for a determination and since there are three ways of pairing these three experiments there result three independent determinations (or if we count both of the alternative ways of interpreting III we really get four independent determinations). Now it appears that each of the three experiments yields results discordant with the remaining two. After the summary of each experiment, therefore, we list just how large a change in any single factor entering into the experiment would be required to harmonize its results with the other two points on the Bond diagram. In every case the cause of the discrepancy is assumed to be concentrated in one factor alone.

I. X-ray crystal determination of e alone

In this experiment¹⁸ e is computed from the Faraday constant and Avogadro's number. This latter is computed from the experimentally determined density of the crystal and absolute size and shape of its lattice cell. To determine this latter in its turn the absolute values of x-ray wave-lengths as determined with ruled gratings are used. The procedure and its result is summed up in the following formulae and definitions:

$$\begin{split} e &= 2d^3 Q_{\rho} \Phi(\beta) M^{-1} = 4.805 \times 10^{-10} \text{ e.s.u.},\\ \text{where } d &= n\lambda / \{2 \sin \theta (1 - \delta / \sin^2 \theta)\},\\ Q &= \text{Faraday constant,} \end{split}$$

M =molecular wt. of CaCO₃,

 $\rho = \text{density of calcite},$

 $\Phi(\beta)p^3 = \text{vol. of unit cleavage cell where } p$ is the perpendicular distance between any two parallel faces,

 $\delta = 1 - \mu = 2 \times 10^{-6};$ sin $\theta = 0.117$,

 $d_n = d(1 - \delta/\sin^2 \theta)$ is independent of λ and depends only on n,

 $d/d_n = 0.999865$ in the first order.

¹⁸ The following incomplete list of references is pertinent to work related to this experiment; on absolute values of x-ray wave-lengths, Söderman, Nature **135**, 67 (1935); E. Bäcklin, Nature **135**, 32 (1935) and Zeits. f. Physik **93**, 450 (1935); J. A. Bearden, Phys. Rev. **47**, 883 (1935); **48**, 385 (1935). On crystal reflection angles, grating constants, crystal densities and Avogadro's number, Larsson, Phil. Mag. **3**, 1136 (1927); A. H. Compton, Rev. Sci. Inst. **2**, 365 (1931); J. H. Williams, Phys. Rev. **40**, 636 (1932); Bearden, Phys. Rev. **38**, 1389 (1931); Defoe and Compton, Phys. Rev. **25**, 618 (1925), Bearden, Phys. Rev. **38**, 1389 (1931), also references 23 and 24. H. N. Beets, Phys. Rev. **25**, 624 (1925), In order that the results of this experiment shall harmonize with II and III₁ (for significance of III₁, see below) *e* must be lowered to 4.768 which requires a change of 0.75 percent in either *e*, *Q*, ρ , $\Phi(\beta)$ or *M*, or a change of 0.25 percent in either *d*, θ or λ . In order that the results of this experiment shall harmonize with II and III₂, *e* must be lowered to 4.785, a change of 0.4 percent in either *e*, *Q*, ρ , $\Phi(\beta)$ or *M* or a change of 0.13 percent in *d*, θ or λ .

II. The point obtained from e/m and R_{∞}

The Rydberg constant R_{∞} in cm⁻¹ units is given by

$$R_{\infty} = (2\pi^2 e^5)/(h^3 c^2(e/m))$$

where e is in absolute e.s.u. and e/m is in abs. e.m.u. Solving this for e we have

$$e = h^{3/5} \left[c^{2/5} (e/m)^{1/5} 2^{-1/5} \pi^{-2/5} R_{\infty}^{1/5} \right]$$

The measured quantities are enclosed in the square brackets

$$\begin{aligned} R_{\infty} &= 109,737.424 \text{ cm}^{-1} \pm 0.06 \text{ cm}^{-1}, \\ c &= 2.99796 \pm 0.00004 \times 10^{10} \text{ cm/sec.}, \\ e/m &= 1.757 \pm 0.0007 \text{ e.m.u./g.} \end{aligned}$$

In order for the results of II to agree with I and either III₁ or III₂ we must have one of the following changes: either e/m or R_{∞} must be increased 0.73 percent or c must be increased 0.36 percent.

III. Short wave-length limit of the continuous x-ray spectrum

This experiment¹⁹ can be regarded in two ways which we designate III_1 and III_2 . According to III_1 no assumption is made as to the absolute value of x-ray wave-lengths. The theory of the inverse photoelectric effect yields the equation

$$h\nu = hc/\lambda = eV$$
,

 λ is determined from the Bragg equation

$$\lambda = 2d \sin \theta$$
,

but d may just as well be regarded as a function of the electronic charge e by the equation given under experiment I as to take the inverse point of view of that experiment. Thus

$$d = e^{1/3} M^{1/3} [2Q\rho \Phi(\beta)]^{-1/3} = K e^{1/3},$$

where K is a function of measured constants. Eliminating λ and d between these three equations we can solve for e and obtain

$$e = h^{3/4} [2KV \sin \theta]^{-3/4}$$

According to III_2 we assume that the ruled grating measurements give the correct value of λ , then

$$\frac{hc}{\lambda = eV}, \\ e = h [c/(V\lambda)].$$

In order to make this experiment agree with I and II as we have already pointed out V must be increased by 0.25 percent or in Fig. 14 the thresholds must be at W_1 and W_2 , a most difficult thing to accept.

It seems worth while pointing out that more difficulties in reconciling points on the Birge-Bond diagram would be eliminated by a change in the absolute determinations of the x-ray wave-lengths by means of ruled gratings or by a change in the Faraday constant than by any other revisions. The striking agreements between various determinations of x-ray wave-lengths by means of ruled gratings by different workers and by dispersion measurements, notably the one by Bearden using diamond as the dispersive medium are very convincing.²⁰ It is not likely that the Faraday constant can be in error by the requisite amount to explain the discrepancy in question since two completely independent methods of determining it agree very well. We refer to the well-known electrochemical determinations on the one hand and to certain spectroscopic determinations on the other hand whose significance was recently called to our attention by W. V. Houston. This interesting and important check is obtained by comparison of the results of the two spectroscopic methods of determining the specific charge e/m of the electron by the Zeeman effect and by the relative displacement of lines in the spectra of the two hydrogen isotopes. The latter method, which is in reality a determination of M/m, involves the Faraday

¹⁹ Duane and Hunt, Phys. Rev. **6**, 166 (1915); Blake and Duane, Phys. Rev. **10**, 624 (1917); Duane, Palmer and Yeh, Proc. Nat. Acad. Sci. **7**, 237 (1921); J. Opt. Soc. Am. **5**, 376 (1921); H. Feder, Ann. d. Physik **51**, 497 (1929); Kirkpatrick and Ross, Phys. Rev. **45**, 454 (1934); Schaitberger, Ann. d. Physik **24**, 84 (1935).

²⁰ J. A. Bearden, Phys. Rev. 47, 883 (1935); 48, 385 (1935).

constant for the computation of e/m while the former method does not. Now it transpires that when the electrochemical value of the Faraday is used these two methods agree very satisfactorily giving the same value of e/m. This result has been independently obtained in three different laboratories by Gibbs, by Shane and Spedding and very recently by W. V. Houston. We believe this establishes the electrochemical value of the Faraday as free from any error of sufficient magnitude to explain the discrepancy in question.

Of course, the above statements of percentage modifications in measured quantities requisite to harmonize the diagram are based on the assumption that the trouble is entirely localized in one place. It is possible that the discrepancy is to be blamed on the cumulative effect of several superposed small errors in several quantities but after careful consideration of such possibilities as applied to points I, II and III we feel inclined to reject them.

Finally there is the possibility that something is fundamentally wrong with the theories at the foundation of these experiments. In experiment I the theory of the diffraction grating with x-ray at grazing incidence seems to have been pretty thoroughly settled by Eckart.²¹ The validity of the x-ray crystal method of determining Avogadro's number seems well established by the experiments of Allison and Armstrong,²² Y. Tu²³ and DuMond and Bollman²⁴ unless perchance one could question the applicability of Euclidian geometry to the crystal lattice so as to vitiate the computation of volume from linear dimensions.

In experiment II it is indeed hard to see how the formula for R_{∞} can be changed by 1 percent and still leave the Balmer formula with all of its well-known accuracy. Modifications in the formula for R_{∞} yielding a relative change of the order of α^2 may indeed be possible but what seems needed is something more nearly of the order of α . The authors are in close contact in this laboratory with highly reliable workers who have repeatedly determined (e/m) both by deflection²⁵ and spectroscopic²⁶ methods and we can find no loophole in this quarter either of a theoretical or experimental nature sufficient to explain the required change of about 3/4percent.

As for the theory of experiment III only the conservation of energy in elementary processes seems to be involved. Elsasser has pointed out that since experiment III is the only one which involves relativistic velocities it is here that one feels a theoretical modification is most likely to be necessary. Such a modification must be of a most fundamental nature to explain, if possible with retention of the conservation of energy, what now appears to be a conversion of electron energy into photon energy at the highly favorable efficiency of 100.25 percent.

We are thus faced with a dilemma which we feel should be very seriously considered both by theoretical and experimental physicists.

The authors consider the present experiment as merely preliminary and they project a much more thorough continuation of this work both at higher and at lower voltages and with better spectral resolution. The latter will be made possible by the recent completion of an extremely powerful source of x-rays. In the quantum law usually written $eV = h\nu$ which should to conform with the quantities actually measured be written $\lambda V = (hc/e)$ it will be interesting to see whether each member of the last equation is really a constant strictly independent of λ and V over a wide range of these variables.

The funds for this investigation were derived from the gift of Dr. Leon L. Watters of New York City for research work in x-rays and atomic structure known as the Watters Memorial Research Fund given by Dr. Watters as a memorial to his wife, Frances Hayes Watters. We are grateful for this opportunity to express our deep appreciation of his gift.

²¹ C. Eckart, Phys. Rev. 44, 12 (1933).

²² Allison and Armstrong, Phys. Rev. 26, 701 (1925). See Allison's excellent discussion of these points in Compton and Allison's X-Rays in Theory and Experiment, p. 698. ²³ Y. Tu, Phys. Rev. **40**, 662 (1932).

²⁴ DuMond and Bollman, Phys. Rev. 50, 524 (1936).

 ²⁵ F. Dunnington, Phys. Rev. 43, 404 (1933).
 ²⁶ Campbell and Houston, Phys. Rev. 39, 601 (1932); Kinsler and Houston, Phys. Rev. 45, 104 (1934); 46, 533 (1934).