

A DEVELOPMENT OF SPECTROSCOPIC TECHNIQUE IN THE
SOFT X-RAY REGION, WITH A TYPICAL SPECTRUM OF BARIUM
AND ITS QUANTUM MECHANICAL INTERPRETATION

Thesis by
Howard Stanley Seifert

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I. ABSTRACT

A concave grazing incidence spectrograph for the long wave x-ray region 40-400 Å is described, together with the technique of operation and some preliminary results of its use. This includes trials of three types of targets, bulk, evaporated and electro-plated, as well as a study of the emission characteristics of four types of oxide-coated dull emitter. A solid nickel box, coated by spraying and indirectly heated by a tungsten helix, was found to operate most satisfactorily.

A discussion of the difficulties of obtaining vacua better than 10^{-6} mm. Hg. in a demountable metal x-ray tube is given, together with some devices for obtaining such vacua. Use of an ionization gauge of special design revealed that the emission in the tube was exceedingly sensitive to pressure of residual gases.

Schumann plates of lines from carbon, beryllium, strontium and barium were obtained, together with microphotometer curves of their contours, which in the case of barium revealed the characteristic symmetry of a transition between non-conducting atom shells. The theoretical significance of these contours is briefly discussed, together with an outline of the quantum mechanical method involving the use of Brillouin zones and the method of self-consistent fields for calculating energy level distributions for both loosely and tightly bound electrons.

II. INTRODUCTION

a). Historical:

The spectral region with which this work is concerned, from about 40 to 400 Angstroms, formed a gap between the optical spectrum and the ordinary x-ray spectrum which has only recently been closed. Spectra in this range are accessible only by means of a vacuum spectrograph, as most radiation from 1800 \AA° down to about 3 \AA° is strongly absorbed in air. Schumann¹ first observed wavelengths as low as 1200 \AA° , using a fluorite prism in vacuum. He also first devised the indispensable non-absorptive photographic materials which have high sensitivity to these radiations. Using a concave grating at normal incidence, Lyman² next measured lines at 500 \AA° . Millikan and Bowen³ then used the "hot-spark" source, which provided lines in a normally barren spectral region, and pushed the limits of optical spectra down to 150 \AA° . During this time, the maximum x-ray wave length observable with crystal spectrometers was of the order of 15 \AA° , limited by absorption in the crystal and the difficulty of getting crystals with a large lattice spacing. Finally Thibaud⁴ in 1926 closed the gap between 15 and 150 \AA° , using a plane grating at grazing incidence (1° to 2°).

The use of highly oblique incidence makes it possible to use ruled gratings in which the grating space

is large compared with the wavelength, and in addition increases the reflectivity of the grating, since glass has an index of refraction slightly less than unity for x-rays in this region and total external reflection may be secured at glancing incidence. Compton⁵ was among the first to use this device for totally reflecting x-rays, which makes possible the use of optical gratings in x-ray spectroscopy. Since 1926 a large amount of work has been done in this region by Siegbahn, Magnusson, Sodermann, Prins, Osgood, and many others, the results of which are tabulated up to 1931 in Siegbahn's book⁶. Concave gratings, introduced by Osgood⁷, are frequently used in the later work, combining speed with high resolving power.

b). Line Contours:

The structure of x-ray lines, that is, variation of intensity with wavelength across the width of the line, is of particular interest in the case of soft x-rays from solid targets, as will be discussed in detail in a later section. Theoretical discussion of this structure is limited to the original calculation for the shape of Be K by Houston⁸, and a few more recent and detailed papers by Jones, Mott & Skinner⁹, Prins¹⁰, and Kronig¹¹. The earlier experimental work was on the structure of carbon K by Renninger¹² and of K radiation from B, Be, C, O, A and Cu by Sodermann¹³. Later Glocker¹⁴ and Siegbahn¹⁵ made a

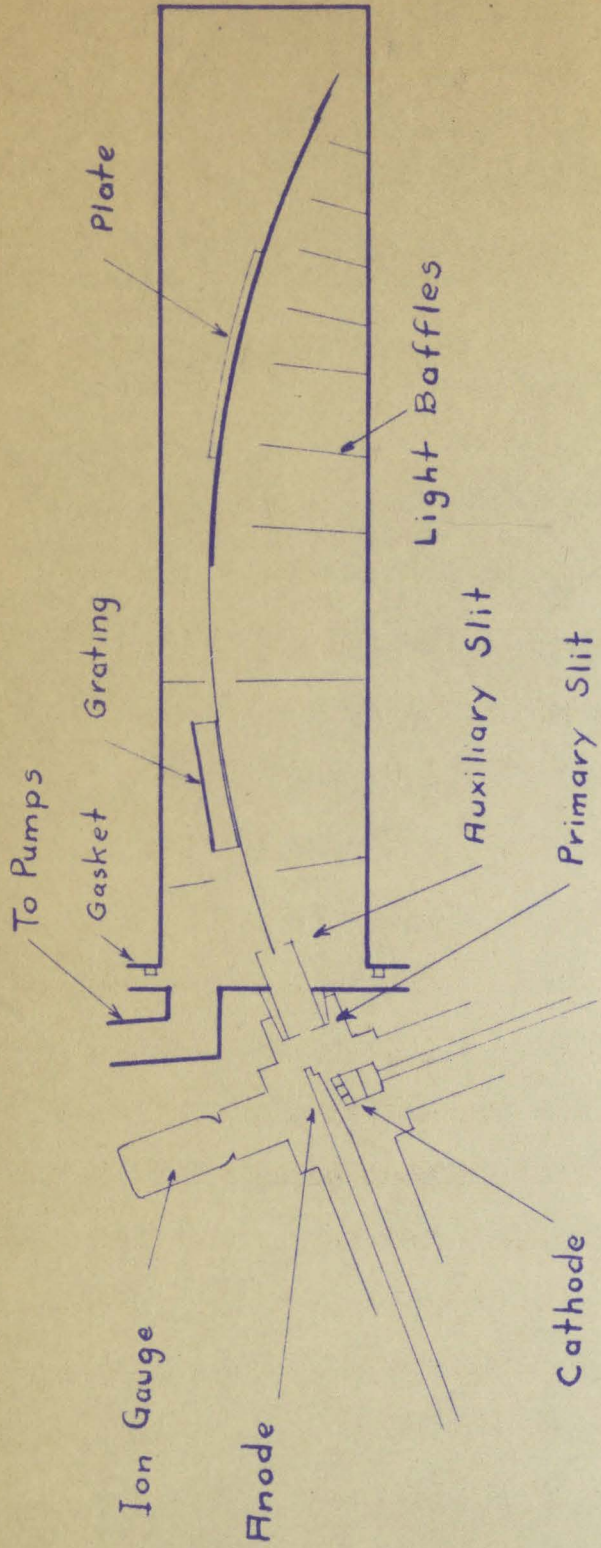
rather extensive investigation of the effect of the various compounds of carbon on the structure of the K line. More recently Hautot¹⁶ and O'Bryan and Skinner¹⁷ have investigated a number of the light elements from atomic numbers 3 to 14. O'Bryan and Skinner's work is noteworthy in that the targets used were frequently re-coated with clean metal by evaporation, a most important detail where easily absorbed radiations such as these are concerned. O'Bryan has also published a paper¹⁸ on the absorption edges of Li and Mg in the soft x-ray region which is of interest for structure data. More recently Skinner¹⁹ has extended this work.

c). Objectives:

Up to the present, most work on line structure has been done with the strong K or L radiation of elements 1-17. For elements 18-35, the radiations which fall within the "soft" x-ray range are those of the M and N series which are much weaker. It is the objective of the program of research of which this particular investigation is the beginning, to photograph as many as possible of the lines--more properly bands--whose wavelengths lie between 40 and 400 A° of elements 18 to 35, that is of the first long period of the periodic table.

The structure of these lines would be of interest as would be a confirmation of the existence of the M and N series for the first long period. So far as the

writer has been able to ascertain, they have never been unambiguously³⁰ photographed, although diagram lines (theoretically possible ones) exist. It is entirely possible that the high absorbability of these lines, which makes them very susceptible to target surface impurities, together with a relatively small transition probability compared to the K and L radiation, and even perhaps some mechanism like the Auger²¹ effect, combine to make their intensity exceedingly feeble. The structure of these bands if obtained, might provide a starting point for the theoretical calculations of line shapes, and in particular the discrimination between the energy level distributions of conductors, semi-conductors, and insulators²².



Spectrograph - Schematic Diagram

Figure 1

III. DESCRIPTION OF APPARATUS

a). Spectrograph:

A 2 meter radius concave grating mounted on a Rowland circle and set at $6^{\circ}14'$ incidence was used, the whole being mounted in a long steel cylindrical vacuum chamber bolted and sealed with a rubber gasket, an arrangement similar to that of Siegbahn²³. The schematic diagram of the instrument is shown in figure 1. The glass grating, ruled by Mr. Julius Pearson at California Institute, had 960 lines/mm and an effective opening of about 4 cm. The slit was used at .25 mm aperture in an effort to obtain short exposure times, and at the glancing angle used, this permitted a resolving power of only 3 mm on the plate (3 to 4 angstroms). However, as the bands being looked for were of the order of 10 \AA° broad, this was adequate for a preliminary survey to determine their existence. The spectrograph was very rigidly built upon a heavy steel girder as a foundation and was capable of resolving sharp lines separated by .03 to .04 A° . It had been adjusted to critical focus by Prof. I. S. Bowen, who had previously used it for a much more exacting investigation²⁴, and the writer did not change this adjustment, using the grating in situ.

Schumann plates on thin ($\frac{1}{2}$ mm) glass were used because of their sensitivity to radiations in this wavelength range, although they are very unsatisfactory for

photometry as Farineau²⁵ has recently shown. For more quantitative work, it may be possible to overcome the marked surface irregularity and lack of uniformity of the Schumann plates (due to the scanty proportion of gelatine in the emulsion) by the use of Ilford Q or some similar type plate. These have a gelatine layer of normal thickness, but specially rich in silver bromide at the surface. The plates are protected from fog by a system of numerous baffles, arranged to cut out any direct light from the slit or the central image and abate reflected light. Only one test for fogging was made, and that did not prove that the light from a simple tungsten filament prohibited its use, but tungsten filaments were abandoned for other reasons stated later. Thoraeus²⁶ mentions an interesting device for eliminating fogging by sending the electrons through an aluminum foil before they reach the target.

b). X-Ray Tube:

The target was a 3" x $\frac{1}{2}$ " diameter copper rod, drilled out for water cooling and cut with an oblique plane surface as shown in figure 2. This surface was coated with the substance being investigated and was subject to electron bombardment. The copper section was silver soldered to a long nickel tube, thus making it possible to heat the entire copper block to redness without conducting too much heat

X-Ray Tube Detail of Anode Assembly and Adjustment

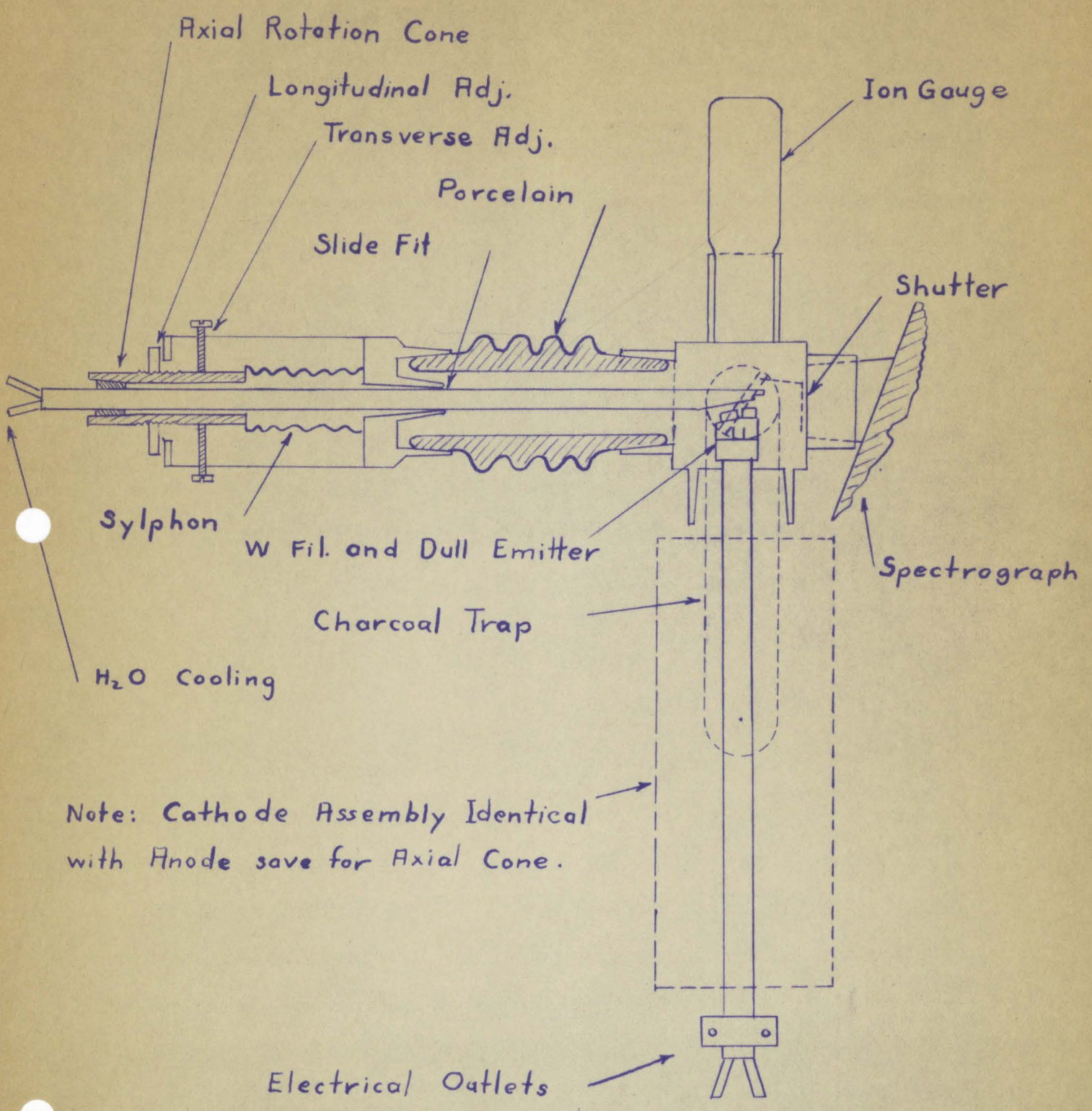


Figure 2

X-Ray Tube Electrode Detail

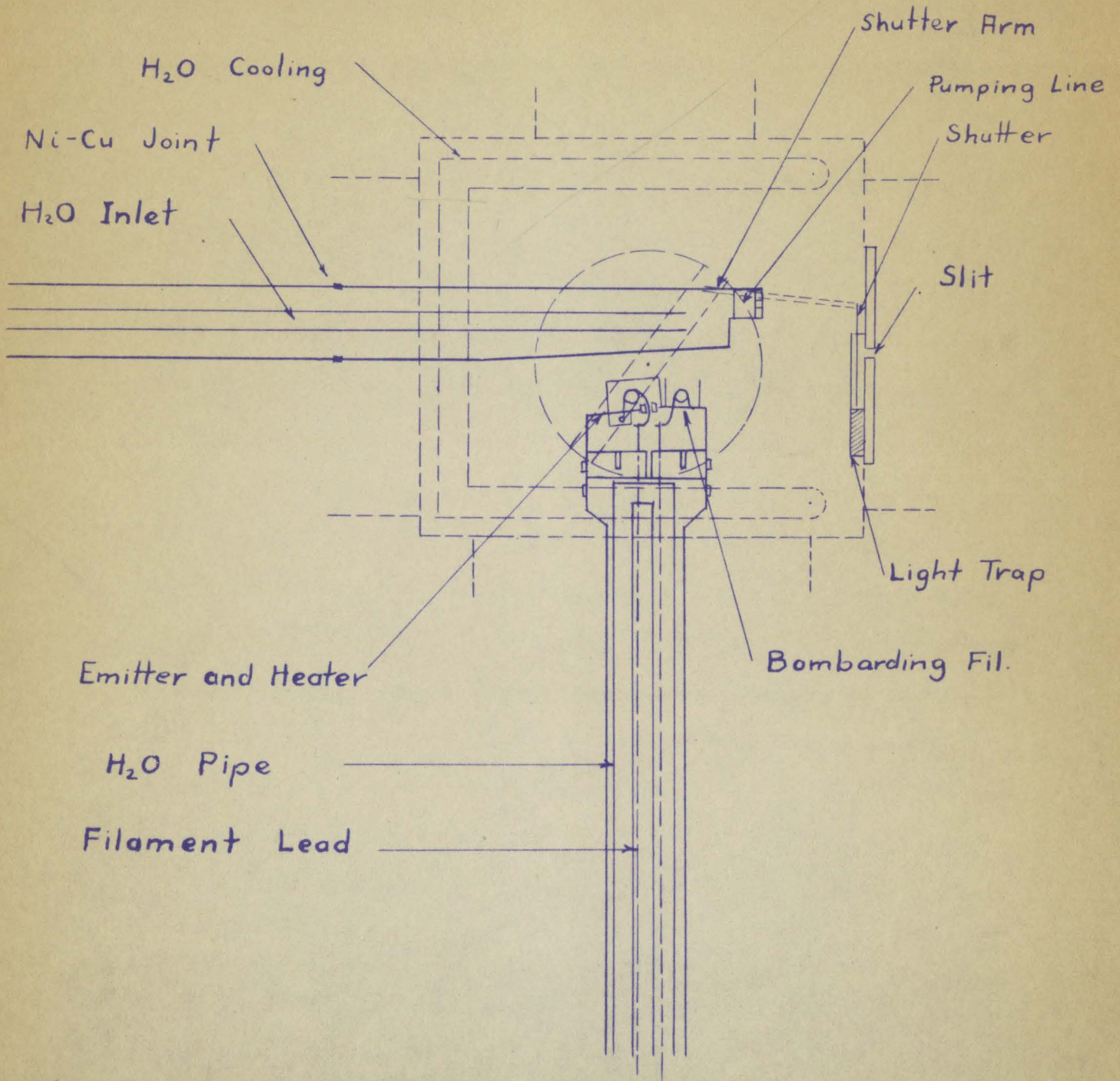


Figure 3

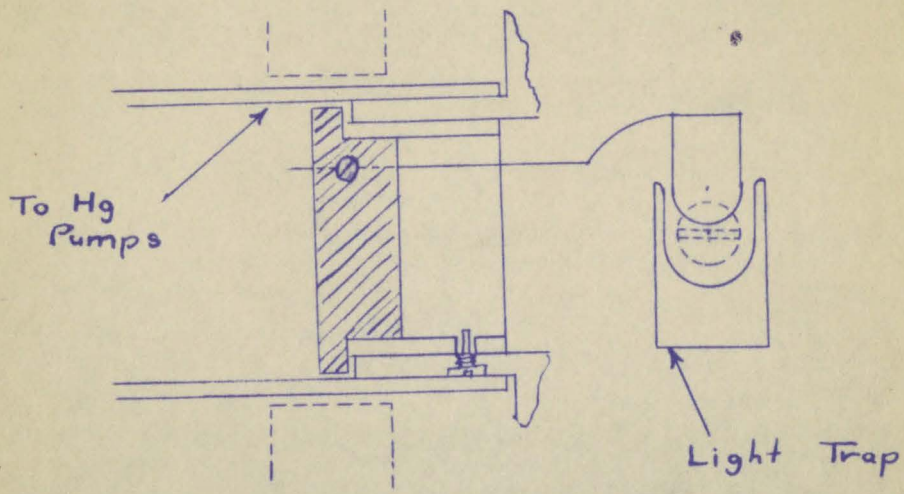
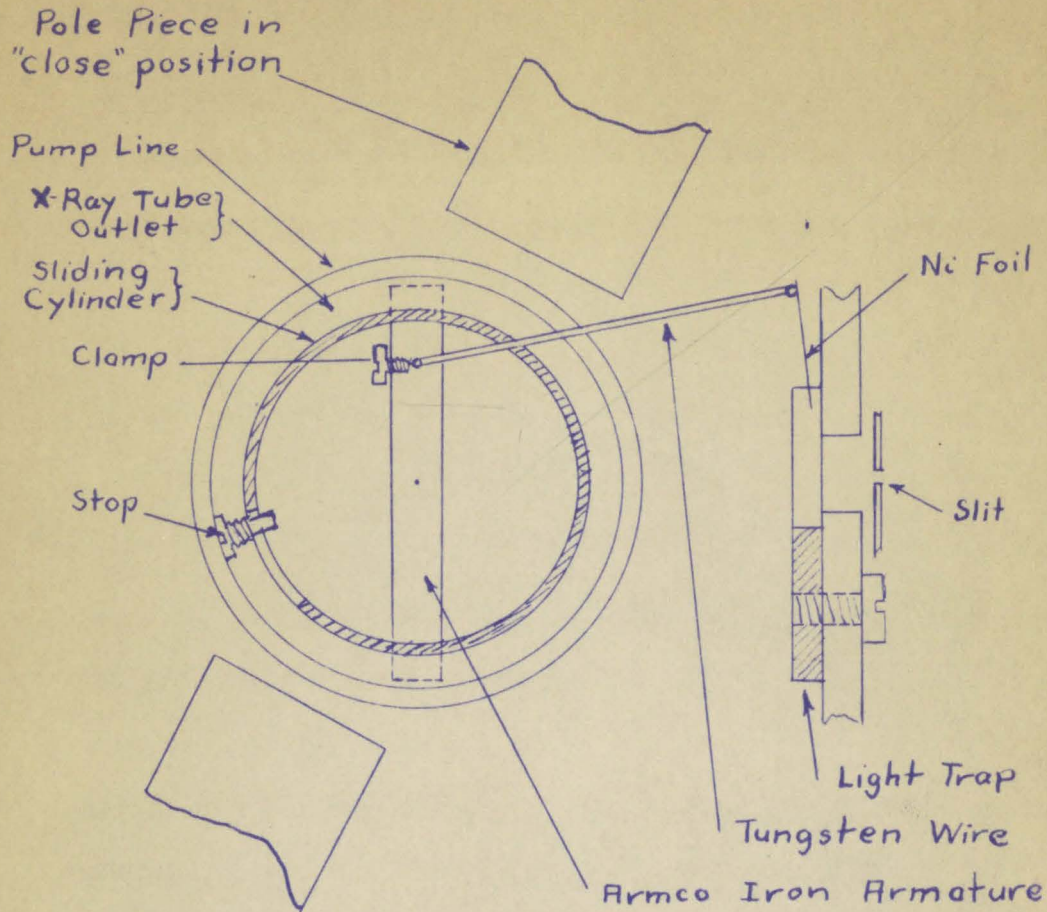
to the point of support of the anode. At the supporting end, this nickel tube was provided with a brass to brass conical ground point, allowing the target to be rotated freely. The entire assembly was water cooled and mounted on a sylvphon, thus providing practically four degrees of freedom for the target, a great convenience in making adjustments. This manner of making these adjustments may be seen from figure 2.

The cathode mounting was water cooled and adjusted in a manner similar to that of the anode, save that no greased cone was used. It provided for two filaments, one a plain tungsten spiral, with radiation shield for use in out-gassing by electron bombardment, and one an oxide coated dull-emitter. This low temperature emitter was adopted after extensive trials were made with three other types of emitter. It consisted of a small box of .022" Ni, coated on one face with a mixture of Ba and Sr carbonates, and indirectly heated by a tungsten spiral inside. The details of the emitter, as well as its position relative to the anode, are shown in figure 3. No attempt was made to focus the electron beam, the spacing of box and target being such that electrons moved in practically straight lines to the target and covered an area about equal to that of the coated face of the box. This area was chosen such a size that the aperture of the grating was just filled. The

target face had a slope of about 1:11 with respect to the direction toward the grating and this made a "focal" spot of about 11 x 7 mm. The oxide emitter was chosen because it produced very little actinic light, and under proper operating conditions should give a high emission with but small evaporation. Tungsten filaments are not only exceedingly brilliant, but at temperatures where copious emission is obtainable evaporate a dense absorbing layer of tungsten on the target, masking the original surface. Thoriated filaments were not tried, but might operate at sufficiently low temperatures to be usable. Both thoriated and oxide emitters are exceedingly susceptible to "poisoning", and require vacua of 10^{-6} mm Hg or better to operate efficiently and without perceptible evaporation. The writer did not find it possible to obtain emissions of 400 ma from these oxide emitters, as was mentioned by Sk & O'B²⁷, but this may have been due to insufficiently low pressures or small active areas.

The x-ray tube elements were mounted in a hollow brass cube about $2\frac{1}{4}$ " on an edge, drilled for water cooling and provided with large circular apertures in each of the six faces of the cube. Two of these, $7/8$ " in diameter, led to pumps, two held porcelain supporting insulators for anode and cathode, sealing-waxed into cones, and the remaining two led to ionization gauge and spectrograph slit res-

Shutter Detail



Side View

Figure 5.

pectively. There were four joints of beeswax-rosin in the complete tube assembly, since the various parts of necessity had to be quite demountable. These joints were a source of considerable trouble because of their lack of mechanical strength and were always the first suspects in case of leaks.

It was necessary to insert a shutter across the spectrograph slit, to avoid fogging when the bombarding filament was in use. This consisted of a brass cylinder bisected diametrically by a small soft iron vane, to which a light shutter of nickel foil was attached by a stiff but light tungsten wire. The whole was mounted inside one pump-line and operated from outside the evacuated system by means of a magnet, as shown schematically in figure 5. In subsequent modifications of this x-ray tube it would be very advantageous to provide more rigid mechanical support for the elements of the tube to supplement the present beeswax joints. As now designed, the tube could be readily adapted to evaporating technique by substituting an evaporating unit in the aperture now occupied by the ionization gauge. It might than be desirable to arrange a magnetically operated shutter in the interior of the spectrograph itself, as the present shutter is frail, tedious to adjust, and susceptible to gumming by vapors and evaporated or sputtered materials.

c). Vacuum System:

The x-ray chamber and the spectrograph were

evacuated by separate Hg pumps, leading into a common Hg pump which acted as a 1st stage, and thence to an ordinary rotary fore-pump (Hyvac). The pumping line to the x-ray tube was 6 ft. of 1" glass tubing, which consequently formed a rather slow system and had to be supplemented by a charcoal trap opening into the opposite side of the x-ray tube. This addition reduced the minimum pressure obtainable from about 10^{-5} mm Hg to below 10^{-6} mm Hg. The charcoal trap was provided with a plane surface which served as a window to observe the position of the tube elements when adjusting.

While the use of charcoal provides very fast pumping, it has a number of disadvantages. Charcoal must be kept completely covered with liquid air or it regurgitates air into the system, and must be baked out to 400°C after each exposure to any pressure higher than 1 mm.Hg. With charcoal it is impossible to test for leaks by allowing the system to stand as the charcoal either absorbs or out-gasses, and cannot be held stationary. It was thought that during the bake-out process condensed vapors emanating from the charcoal might be deposited throughout the x-ray tube, but in two runs made specifically to test this point no effects of vapor could be found.

Attaining the necessary pressures of 10^{-6} or lower proved to be one of the major difficulties of the experimental work, and at least one-third of all the time spent in the laboratory was used in hunting for leaks or waiting for residual gases and vapors to pursue their lei-

surely and statistically random course into the limbo of pumps and traps. Some trouble was experienced with ground brass anode cone, on four different occasions rotation of this joint caused large leaks. It was finally reground and lubricated with Apiezon L, a special low vapor pressure vacuum grease.

If the system was tight, pumping for 12 or 15 hours was sufficient to bring the pressure in the x-ray tube down to slightly less than 10^{-6} mm Hg. It was found possible to reduce the pressure in the x-ray tube to a few multiples of 10^{-7} mm Hg by separating it from the spectrograph. The pressure in the spectrograph was undoubtedly much higher than in the x-ray tube, probably between 10^{-4} and 10^{-5} at best. However the small slit area ($1\frac{1}{2}$ sq mm) prevented any excessive flow of gas between the two chambers* at low pressures. In order to facilitate long (overnight) periods of pumping without attendance on the Hg pump, a heater switch which opened automatically when the water circulation stopped was installed. This could be rendered more reliable by the installation of a sediment filter in the intake side of the water system. A large 1 cm bore cutoff mercury seal stopcock was inserted between the spectrograph and the first stage Hg pump, a very useful adjunct in testing for leaks.

*See sample calculation in appendix.

Pirani Gauge Wiring Diagram

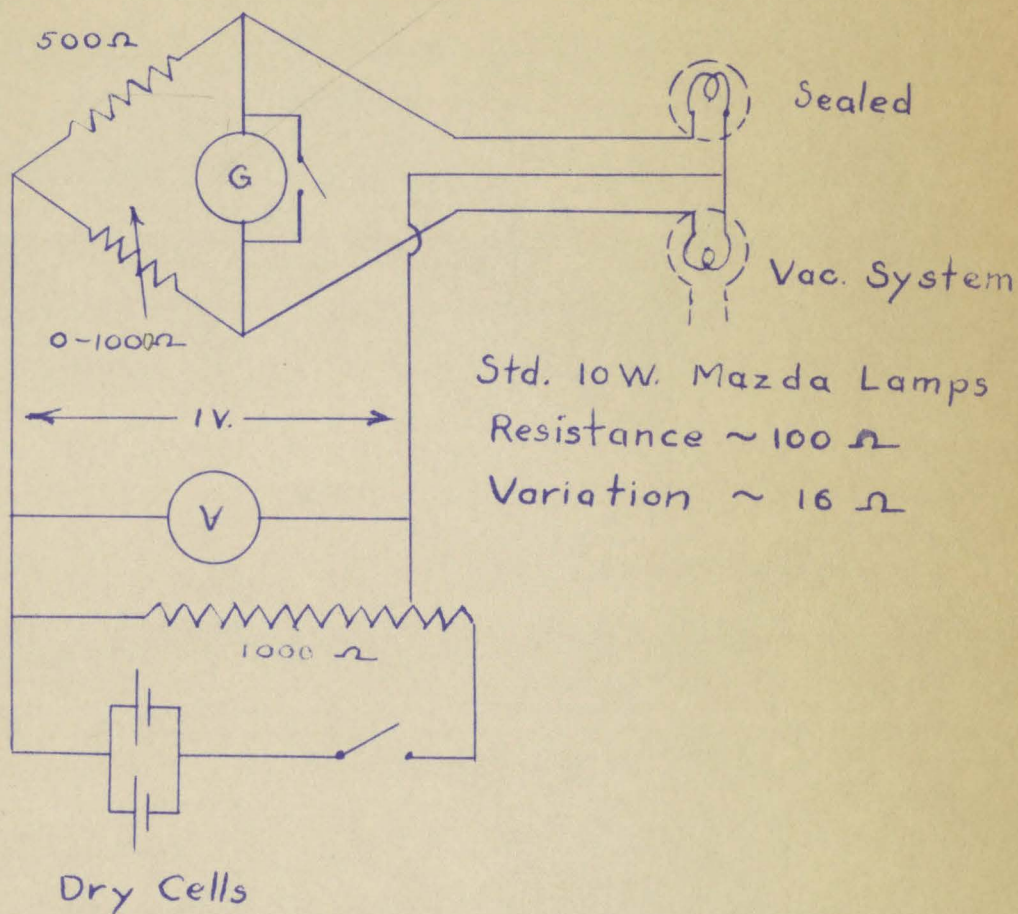
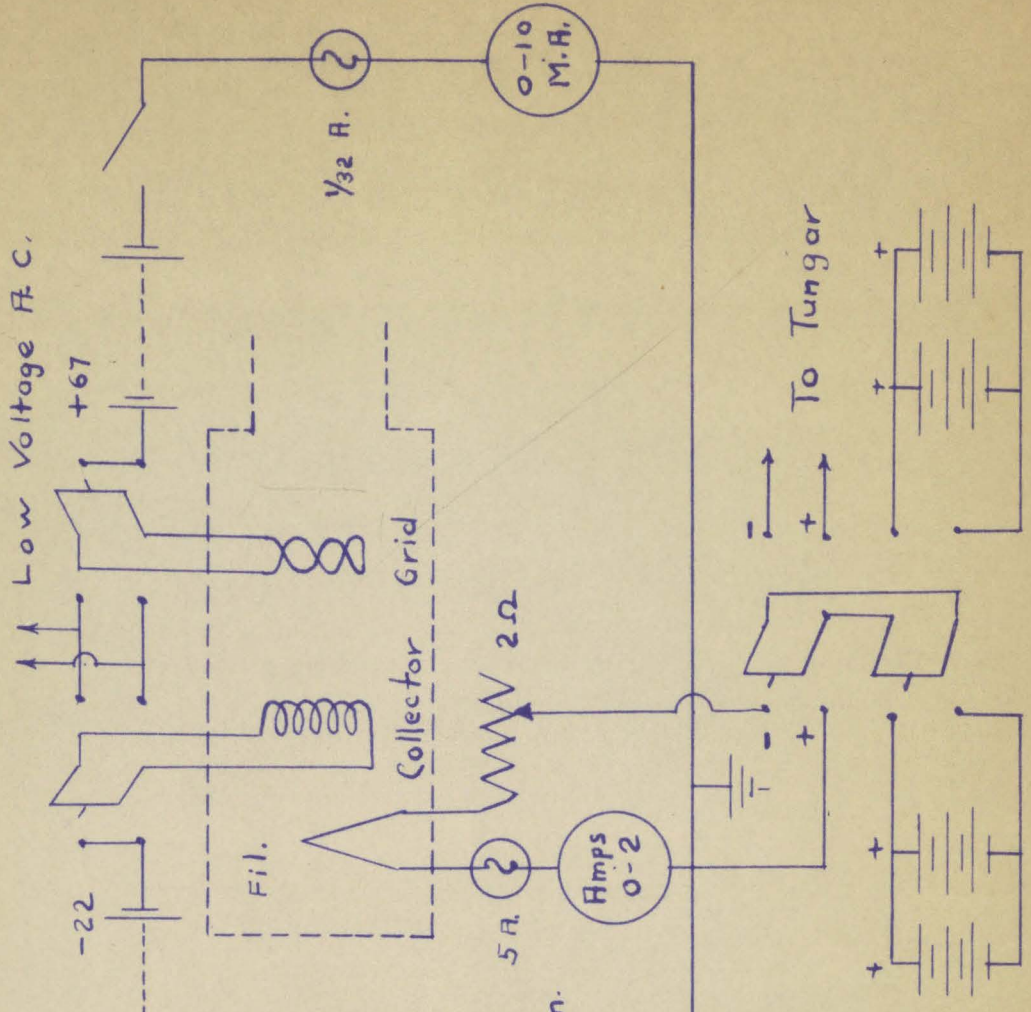


Figure 6.

d). Manometers:

Any experiments involving the use of oxide coated cathodes require very careful control of the pressure, hence a manometer which will discriminate definitely between 10^{-5} and 10^{-6} mm Hg is an essential part of the apparatus. At first the necessity for absolutely optimum pressure conditions was not realized, and a Pirani²⁸ type of hot-wire manometer was built, having a useful range from 10^{-1} to 10^{-5} mm Hg. This gauge, while quite inadequate to indicate differences between pressures of 10^{-5} and 10^{-6} , was still of great utility in hunting leaks and indicating when conditions were safe to use the delicate ionization gauge. The wiring diagram and construction data of the Pirani gauge is given in figure 6. A and B are two ordinary ten-watt bulbs, one of which is tubulated and open to the region to be measured while the other is left sealed. The sealed bulb tends to balance out errors due to temperature changes. Actually, when standard light bulbs were used, random fluctuations in temperature due to irregular thermal contact between filament and metal supporting hooks produced errors amounting to 10% of the total change in resistance of the filament. This greatly reduced the reliability and range of the gauge, for between 10^{-4} and 10^{-6} the change in filament resistance is very small. A discussion of the merits of this gauge is given by DuMond²⁹.

Ionization Manometer Wiring

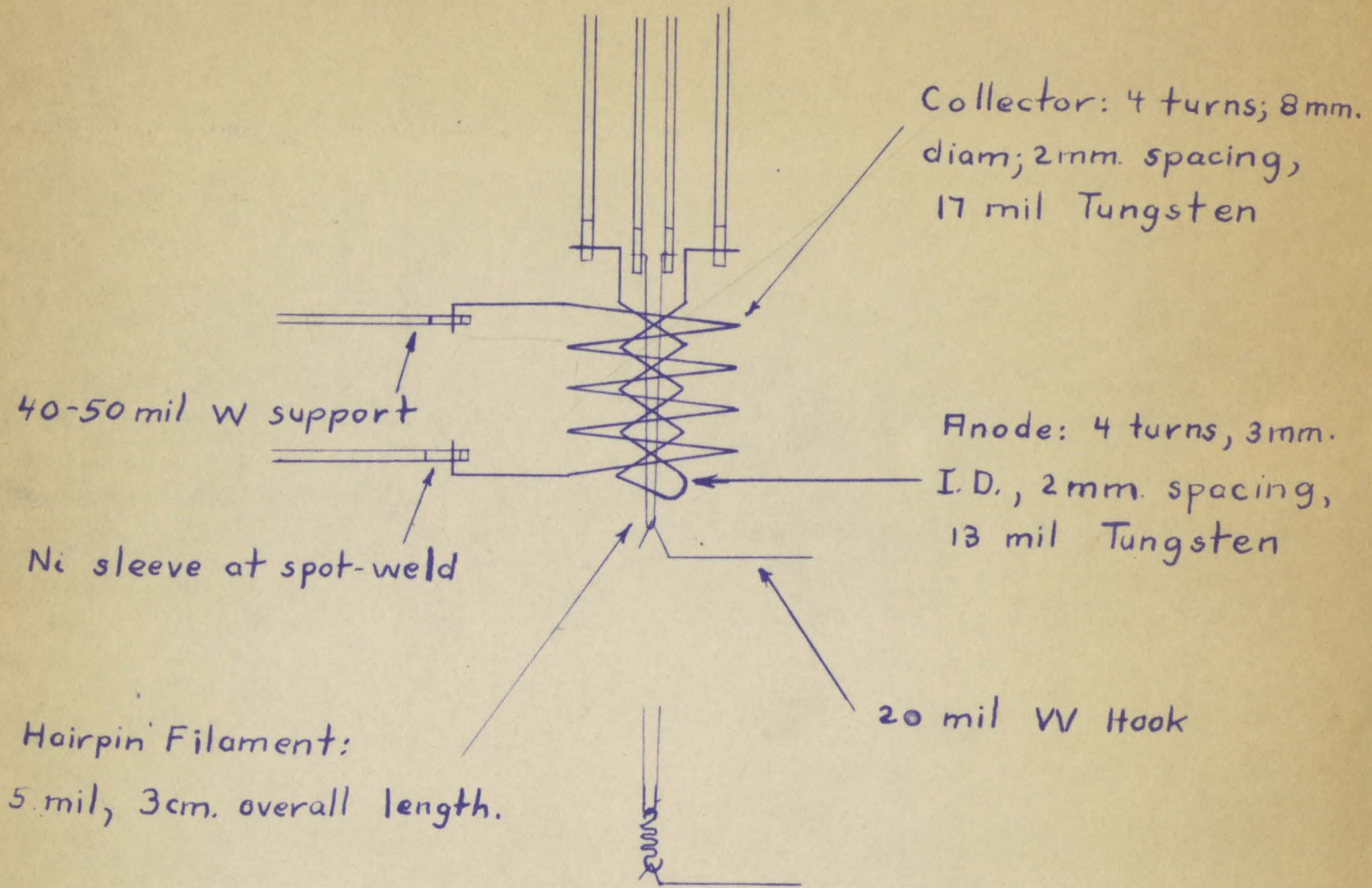


18.68 Ω = 100 Shunt
 205.6 Ω = 1/10 "
 R. Galv. = 1850 Ω (Nominal)

"B" Bank
 6 V. Storage - Charge at 3 R. per Bank
 "H" Bank

Figure 8.

Ionization Gauge Electrode Assembly



Suggested Change

Figure 7

After it was realized that barium oxide emitters operated inefficiently and evaporated badly at pressures greater than 10^{-6} , an ionization gauge was installed. This gauge, of which the elements are shown in figure 7, is an adaptation of one by Huntoon and Ellett³⁰, and is arranged so that all the elements can be baked out without the necessity of electron bombardment, thus reducing wear on the filament and speeding up the operation of the gauge. The filament was run at 5 milliamperes emission for the sake of high sensitivity. The remaining operating voltages and conditions are given in the wiring diagram, figure 8.

By a fortuitous coincidence, another gauge identical with the writer's was built by Dr. Dunnington in this laboratory and calibrated approximately against a McLeod gauge. This calibration has been adopted by the writer as being roughly correct for his own gauge, as the gauges are not very critical³¹ as to exact electrode spacing, etc. The shape of the calibration curve merits some attention. In the customary³² ionization gauge using a solid plate for a collector, the graph of ion current against pressure is linear, of the form $i = Kp$. In this gauge, where the only departure from the classical construction is in the use of a wire helix instead of a plate for collector, the graph is distinctly non-linear, as the slope of the logarithmic

Fig. 9

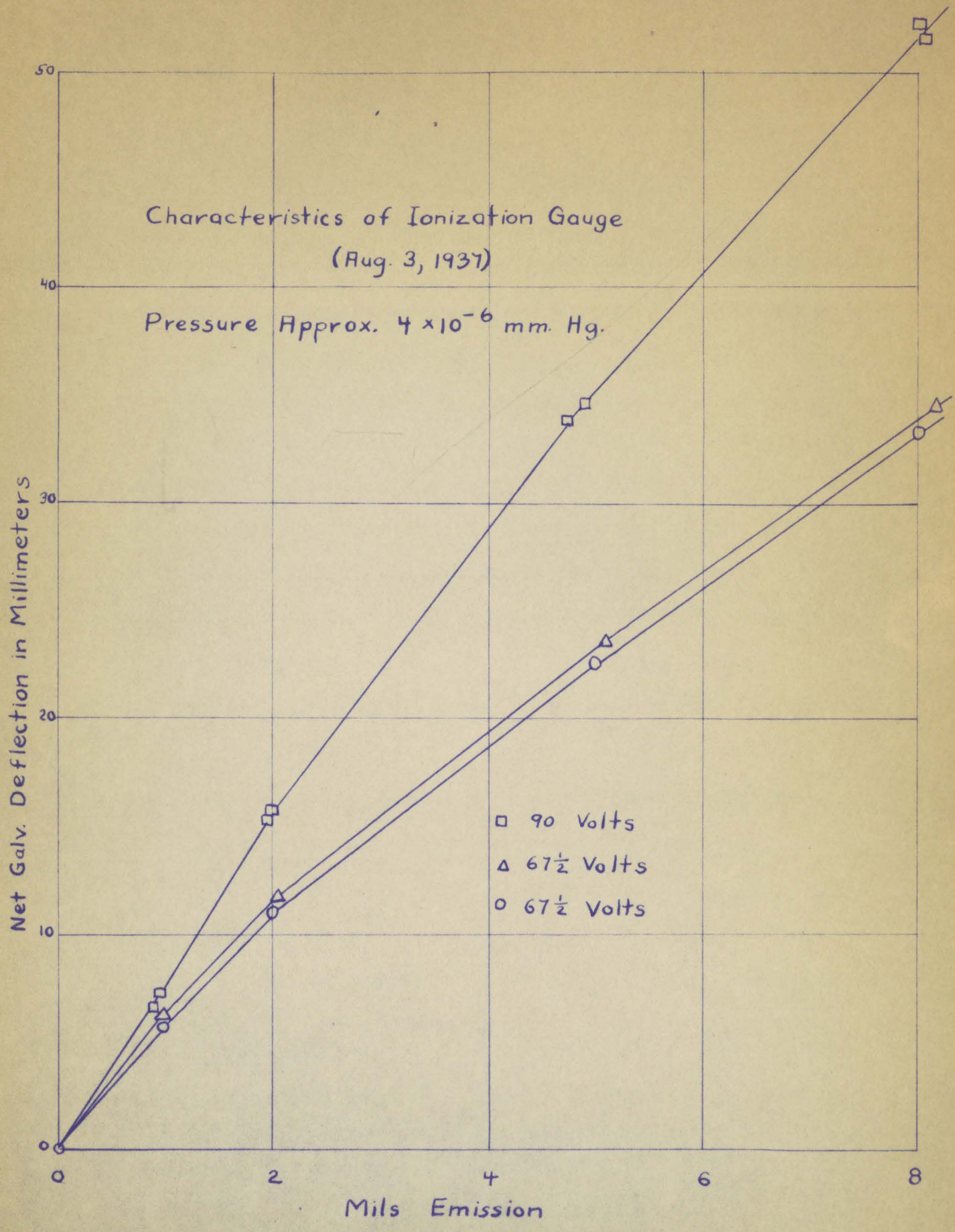


Figure 9.

plot of i against p is definitely not unity. It is difficult to see a reasonable mechanism to explain this peculiarity, but if Dunnington's calibration curve is valid, it is possible that H & E's²⁷ suggested calibration may be entirely incorrect in the pressure range 10^{-4} to 10^{-6} .

Although the ion current was not linear with pressure, it was reasonably linear with electron emission current. The result of tests on this point at two different sensitivities are given in figure 9. Curves (a) and (c) were taken 40 minutes apart, and are as nearly identical as could be expected in view of the fact that no special attempt was made to keep the pressure constant. In general, readings of the ionization gauge taken at consecutive brief intervals agreed to within 1%. The sensitivity was such that a deflection of 1 cm on the galvanometer used corresponded to a nominal pressure of about 5×10^{-7} mm Hg.

The principal random uncertainties involved in the use of the gauge were a) the leakage current through the insulation, and b) unsteady emission from the filament. Leakage currents were of the order of 10^{-8} amps, sufficient to give a leakage current larger than the ion current at the lowest pressures. However the leakage was found to be rather steady, any variations occurring smoothly and slowly over periods of several hours, so corrections could

X-Ray Tube Wiring

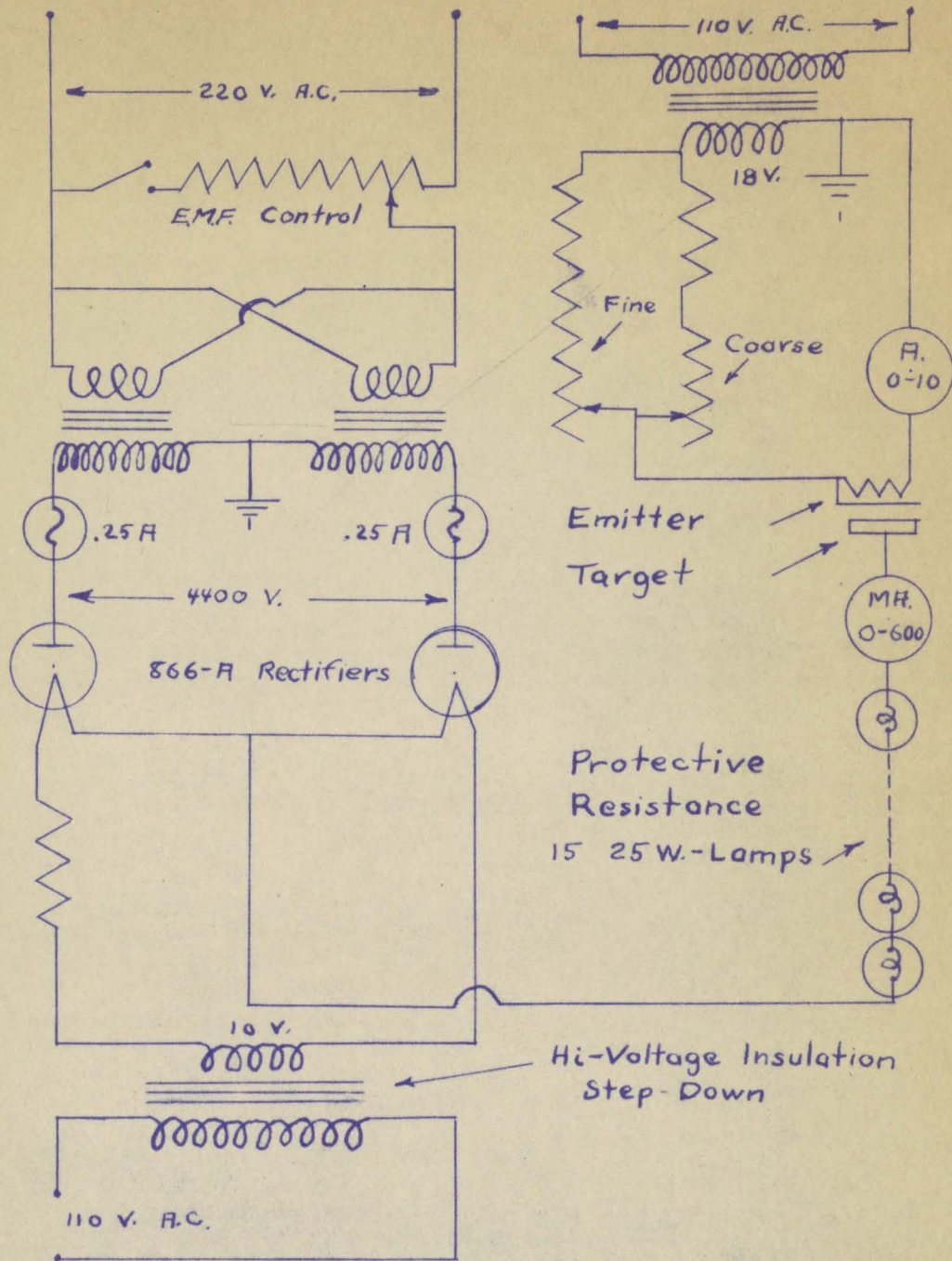


Figure 10

could always be made. The irregular emission was finally traced to an imperfect thermal contact between the hairpin filament and its supporting hook. This caused random (sometimes periodic) temperature fluctuations to which of course the emission was exponentially sensitive. It is suggested that in future models of the ion gauge a spring be inserted to put the filament under definite tension. It is also entirely possible to trace down and eliminate the leakage currents, although such a course did not seem necessary to the writer.

e). Power Supply:

As a source of potential for the x-ray tube 2000 volts of unfiltered, but fully rectified A.C. were used, the output of two RCA 866-A mercury rectifiers and two commercial power transformers with their secondaries in series. The tube voltage was regulated by a variable voltage divider in the transformer primary. Such regulation was found indispensable in controlling the activation of the oxide emitters. A bank of 15 25-watt lamps was inserted in series with the anode, thus preventing large accidental surges of current due to short-circuits or gaseous arcs in the x-ray tube. This lamp bank also served to some extent as a regulator for the x-ray tube, the voltage drop across it decreasing as the current through the lamps increased.

A circuit diagram of the arrangement is shown in figure 10. When in use, the x-ray tube was covered with a fiber hood as a safety measure.

Evolution of the Oxide Coated Emitter

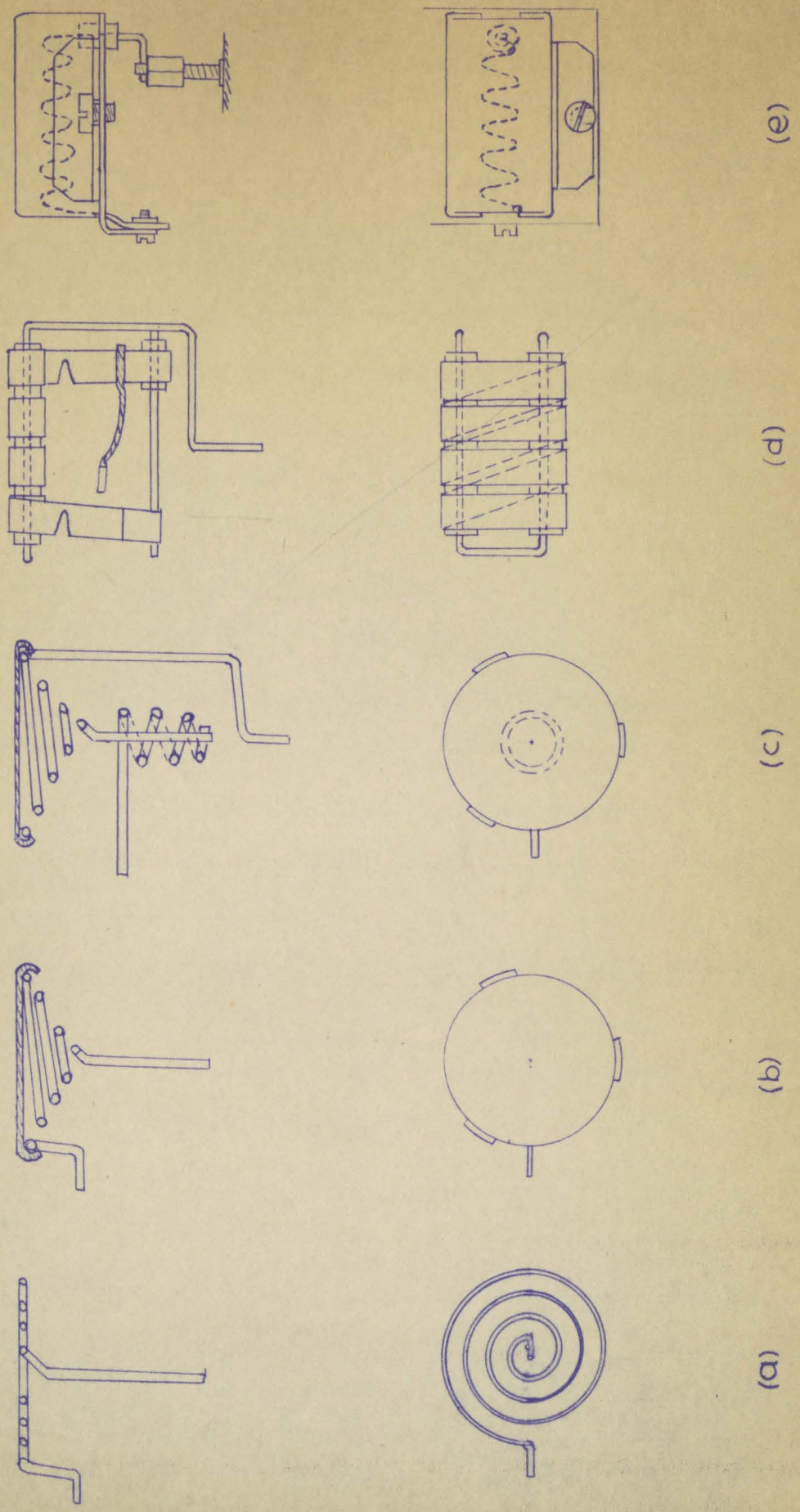


Figure 11

IV. TECHNIQUE OF OPERATION

a). Preparation of Emitters

(1). Heaters:

A large number of different emitters were tried in an effort to get one which would operate efficiently. They can be classified as direct or indirect with respect to method of heating, and as waxed, brushed, dipped, sprayed or electrolytically deposited according to the manner of coating. The heating methods will be discussed first.

A simple flat spiral of the type used in ordinary high voltage x-ray tubes was first tried, but had inadequate emitting area, showed a strong tendency to warp since it was fastened rigidly at both ends, and was difficult to install, as each individual filament had to be cut and bent by trial to fit. Mounting it inside a cylindrical focusing shield with small clearance was a tedious job with considerable probability of a short circuit after warping occurred. Both Ni and tungsten wire were used.

To obtain larger effective emitting area, a flat Ni foil disc was fastened by lugs over a dished tungsten spiral as shown in (b), figure 11. This had, in addition to all the difficulties of the preceding type the disadvantage that it was thermodynamically poor in design, the tungsten spiral having to be heated to a brilliant white

to bring the Ni to a dull orange, with the resultant danger of fogging and unnecessary dissipation of heat. An attempt was made to overcome the warping of these filaments by connecting one end with a flexible lead wire (see ((c)) figure 11) but this failed for lack of a flexible material with sufficiently high melting point.

A more successful type of emitter is shown in (d) figure 11, in which a nickel strap $1\frac{1}{2}$ mm wide and .006" thick was wrapped around two "Usalite" ceramic tubes held on a tungsten wire frame. This emitter had a large surface and could be shaped concave so as to give a line focus, but was not of uniform temperature due to cooling at the ends of the nickel strap. Even after the ends of the strap were cut through 80% of their cross section the cooling was still visibly evident. A flexible connection was successfully incorporated in these emitters because of their low temperature of operation, and appears in the photograph of figure 12. The difficulty which finally eliminated this filament was the fact that after activation, emission would tend to build up from one loop of the filament, whereupon this loop would heat up inordinately (probably due to $I^2 R$ losses in the high resistance coating) evaporation would occur, and in addition the remaining loops would not contribute to the emission, due to their much lower temperature.

An emitting surface of one piece of rather heavy metal would provide more uniform temperature conditions, so recourse to indirect heating seemed expedient. The emitter finally adopted, which has given satisfactory and convenient service, is shown in (e) of figure 11. It consists of a box of .020" nickel, 8 x 12 x 6 mm, held in position by a single 80-0 screw. The heater filament, which is also clamped by a screw, is a 2 mm diam. helix of 16 turns of 15 mil tungsten wire. The relative arrangement of parts is clearly shown in the figure. It was found very advantageous to have all parts demountable, as frequent replacement is necessary. An arrangement immediately preceding this one in which the box was sprung between nickel lugs instead of clamped, and the filament spot-welded in place, was found very inconvenient and hard to adjust. Two of the screw-clamp boxes were made and used alternately, one being coated while the other was in use. A piece of Usalite tubing was used to insulate the heater filament lead, near one end where it was relatively cool, and did not melt or prove gassy, as the box arrangement was so efficient that it could be heated to a bright red when the interior filament was still only at yellow heat. An effort to measure the actual temperature of the box with an optical pyrometer could not be carried out accurately because the amount of absorption by condensed barium on the observing window was not measurable. However these observations gave a lower limit to the apparent tem-

perature, while calculations using the wattage input to the heater and assuming all heat lost by radiation gave an upper limit, between which limits the true temperature must fall. Estimates to the nearest 50 degrees could be made this way which were consistent with the usual³⁴ "color temperature" estimates.

(2) Coating:

The active surfaces of nearly all low-temperature emitters contain the alkali earth metals or their compounds, particularly barium and strontium, and there are numerous references* concerning the coating mixtures. Our first attempt at coating an emitter was to melt Dennison's white sealing wax on it and then heat in air to burn away the organic matter. This method is due to Siegbahn³³. In our case the filaments so prepared were not sufficiently uniform. The same difficulty was found when coating suspensions were mixed in the laboratory following the recipe of Wagner³⁵. The mixtures were not sufficiently smooth and the dried surface would exhibit a lumpy appearance under magnification. These lumps are inevitable loosened when subject to fields of 1000 volts/mm simultaneously with heating, and cause trouble in the x-ray tube by producing bursts of current and glowing impurities on the target.

*See Bibliography.

Consequently an absolutely smooth and firmly adherent coating is essential. Coating by dipping or brushing has the disadvantage that surface tension effects during drying cause the coating to vary greatly in thickness from center to edge of the emitter. When operating, the outer surface of such deposits is cooler at the thick places than at the thin ones, and hence cannot be properly "activated" (made to emit) without overheating the thin portions. Some workers suggest sintering³⁶ the coating in an inert atmosphere of CO_2 to make it firmly adherent. The writer built two different CO_2 furnaces but was unable to heat the emitters without discoloration due to some form of undetermined impurity. Sintering did not seem to be essential to adherence, so it was not pursued further. The electrophoresis (electrolytic deposition from a colloid) process of Patai and Tomaschek³⁷ produced smooth and firmly adherent coats which worked well, but was very complicated and unreliable, hence was abandoned after a few trials.

(3). Spraying:

The most rapid and generally satisfactory coating method was spraying. Since this was the technique used, it will be described in detail. The coating material used was a commercially prepared suspension of BaCO_3 and SrCO_3 mixed crystals in amyl acetate and collodion. A consider-

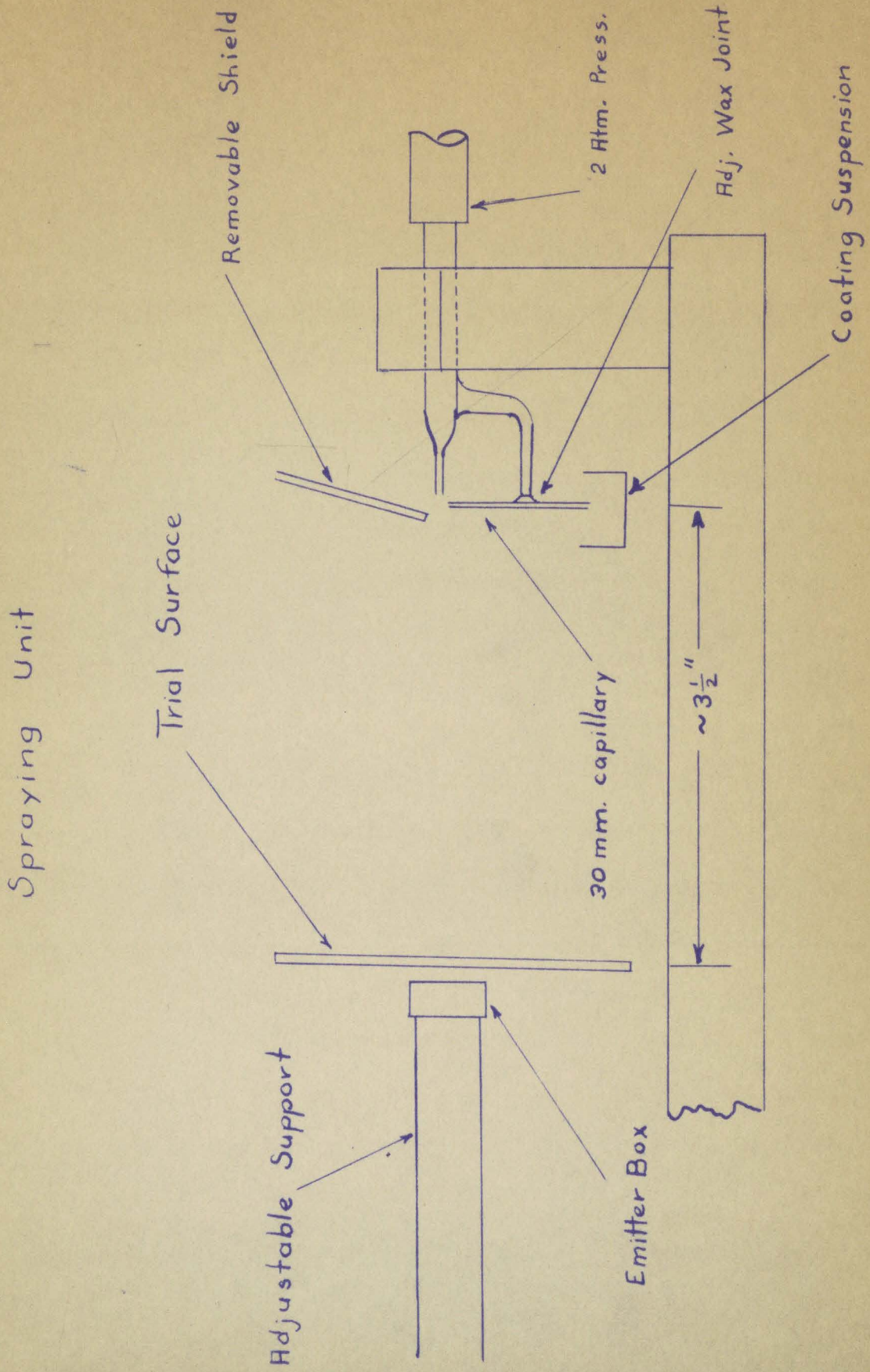


Figure 12

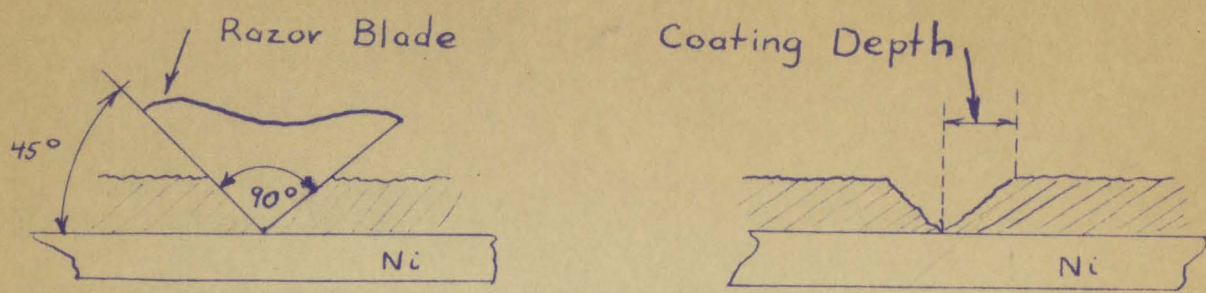
able quantity was supplied gratis through the courtesy of Mr. Shaw of Radio Corporation of America. Before spraying it was well shaken, diluted with twice its volume of amyl acetate, and twelve drops of collodion added to 3 cc of the diluted suspension. This mixture was allowed to settle at least three minutes before use, otherwise lumpy coatings were formed. The atomizer used, shown in figure 12, was designed with small volume to avoid waste. The suction tube was a glass capillary 30 mm long and .2 mm bore.

In actual operation, a jet of compressed air at two atmospheres gauge pressure (measured on a closed tube mercury manometer) was maintained through the nozzle, a small cup of suspension mixture was brought up around the end of the suction tube with one hand, and just a fraction of a second later a glass screen was inserted before the nozzle with the other hand to cut off both air and solution simultaneously. Unless both air and solution are cut off together in this manner the coating dries too rapidly and is uneven. With practise spray "shots" of as short duration as 1/10 second can be produced. Usually one "shot" of 1/10 to 1/5 sec. length was made and allowed to dry, and then another longer one of $\frac{1}{2}$ to $\frac{3}{4}$ second, which spread evenly and with less surface tension deformation because of the presence of the first one. It was necessary to level the sprayed surfaces from their vertical receiving position at

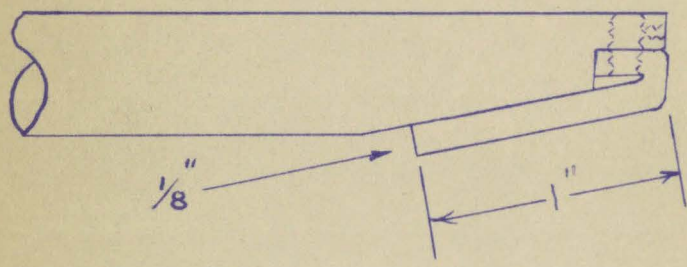
once, in order that settling under gravity not cause the coating to be thick at one edge.

The spray cone was of such a size that the emitter area of 8 x 12 mm was fairly uniformly covered at distances of $3\frac{1}{2}$ to 4 inches. Spraying nearer made the coatings too wet and sedimentary, longer distances tended to make them dusty and granular, with poor adhesion. Naturally degree of dilution, time of settling, thoroughness of stirring, air pressure, and humidity were also factors in determining the nature of the coating, and it was often necessary to make several trials before the optimum conditions were found. To do this a removable glass shield was set up before the emitter on which trial sprays could be inspected. The best coats showed no more unevenness than a carefully painted or enamelled surface, and the surface irregularities seen under the microscope were of the order of 1 or 2 wide.

The thickness of coating recommended in commercial manuals³⁷ is about 40-70 (about 4 to 7 mg/cm²) but the writer found thinner coats of about 20-30 to be more uniform and easier to activate. Longevity was not an important desideratum here, as most exposures were well under 30 hours, and the emitter of necessity had to be recoated after each exposure to atmospheric pressure. While the coating could of course be weighed after each spraying, it



Measuring Approx. Coating Thickness
(a)



Detail of Solid Ni Target
(b)

was found much quicker and still sufficiently accurate to make a small v-shaped groove in the coat at 45° with a specially ground razor blade, (see figure 13) whence a measurement of the half width of the groove on a comparator gave its depth directly to an accuracy of about 15%. A spray under the conditions mentioned above gave coatings from 25 to 40 thick.

b). Preparation of Targets

In a study of a series of elements, each target presents a problem of its own, since the vapor pressure, melting point, heat and electrical conductivity, ease of oxidation, etc., must be considered separately in each case. This is especially true when it is desired to evaporate the target materials. A remarkably complete bibliography and discussion of the various methods of preparing x-ray targets (excluding evaporation) is given by Muller³⁹. The targets may be classified under bulk materials and films.

1). Bulk Materials:

Since the target itself was of copper, numerous runs were tried with it alone, after polishing it with 4/0 French emery, rinsing with pure absolute alcohol and heating to redness for 1 min. in vacuo. In almost every case an opaque film of barium from the emitter condensed on the bombarded surface, which was water cooled, and a

really adequate exposure of the unmasked copper surface was not obtained. In many of the runs a barium line appeared on the plate at about 167 \AA° , which lay so near the estimated position of the copper M_3N_1 line (164 \AA°) that it was very uncertain whether they could be distinguished even if the latter were present. For this reason it was decided to use nickel for a target, for which the M_3N_1 line position was estimated to lie at 181 \AA° .

The use of soft solder to provide good thermal contact between nickel and copper support was prohibited by the necessity for outgassing at red heat after evacuation. Without this purging the gassy target soon poisoned the oxide emitter. To hard solder the Ni to the Cu was not feasible since it was desirable to make substitutions of target material without injuring the plane face of the rather delicate anode. Consequently a cylinder of .023" Ni was merely wrapped around the Cu anode and clamped. When the attempt was made to heat it to redness by bombardment heat conduction through the relatively thin nickel was so poor that the cylinder melted and vaporized at the point of bombardment before more remote parts had become visibly hot.

To eliminate this trouble a heavier block of Ni, $1/8 \times \frac{1}{2} \times 1$ ", was screwed at one point to the anode. This could be heated to a fairly uniform orange color by

about 20 mils bombarding current at 2000 volts, and it was thought that by maintaining the Ni at this temperature condensation of barium upon it might be avoided. However when activation was actually attempted it was found that the block was very difficult to outgas; moreover thorough outgassing was hindered by another complication. When the Ni was held at an orange or yellow color for longer than a few minutes a dark grey deposit, presumably of evaporated nickel, formed over the white surface of the oxide and rendered the emitter inactive. Consequently the excitation of anodes of the Fe-CO-Ni group at temperatures greater than 700° C by means of oxide emitters does not seem feasible.

The remaining possibility seemed to be running the target as cool as possible, so that both gassing and evaporation would be negligible, and attempt to operate the emitter so efficiently that no evaporation occurred from it either. To this end a copper block was nickel plated and mounted on the target. This block was capable of being bombarded with 100 mils indefinitely without being heated to redness, so long as the anode proper was water cooled, although geometrically it was identical with the solid Ni anode mentioned above. The Ni plating did not peel off under the most intense bombardment, although its polished surface became granular. In spite of the superior cooling of this target, emission could not be maintained against

it from an oxide filament, and pressure measurements showed that the target was gassy. No further efforts with bulk targets were made, although it is possible that by baking the blocks at red heat in an atmosphere of hydrogen for several hours the difficulties due to outgassing could be avoided. Experiments on targets were confined to nickel, but presumably any method which succeeded for nickel could be applied with but little change to cobalt and iron.

The only insulator used as a target was bromine in the form of KBr. For bromine a line is recorded at 193 \AA by Siegbahn⁴⁰. The fused KBr (at 700° C) could not be flowed upon a copper supporting surface as it apparently reacted with the copper with resulting red discoloration and poor adhesion. However it was possible to dip a strip of nickel into a bath of molten KBr without undue oxidation, then heat the whole until the KBr layer had flowed off to the "proper" thickness, which was set arbitrarily at about $\frac{1}{2}$ to $\frac{1}{4}$ mm. Thicker coatings showed a tendency to crystallize and crack, and all coatings were very hygroscopic. The resulting coated strip was tinned on one side and soft-soldered to the copper anode, hence baking out to redness was not possible. Accordingly the resulting target was too gassy for use with oxide emitters and no run was obtained. Even if the outgassing of such a target were successfully

accomplished, the bombarding currents would be limited because of the poor heat conductivity of the insulator and its ease of evaporation (melting point KBr 700° C). This trouble with evaporation was especially noticed when an attempt was made to prepare a KBr target by heating a Ni strip covered with loose KBr crystals in vacuo. The KBr evaporated without appreciably wetting the nickel. Even when an atmosphere of 10-20 cm of H_2 was supplied, target preparation by this method was exceedingly critical, and only one target was completed. A further difficulty which might be anticipated with non-conducting targets is the building up of surface charges which would reduce the effective potential of bombardment. Possibly these difficulties may be overcome by the use of very thin insulating layers or by forming compounds between the insulating material and the anode surface itself, which would be precipitated on the anode in a thin film.

2). Metal Films:

Distillation of the target substance in a good vacuum upon the copper anode has several desirable features. The metal deposited is gas-free and clean, and in addition to giving a true spectral line, tends to inhibit gassing from the metal beneath. Moreover it is well cooled, being in intimate contact with the water cooled copper anode, and consequently does not of itself evaporate. By renewing such

surfaces at frequent intervals, Skinner and O'Bryan⁴¹ obtained very satisfactory line contours for the light elements. The writer attempted to repeat their work on beryllium, but at the time had not developed an anode which could be heated to redness, and found that the beryllium did not adhere well to copper unless it had been thoroughly outgassed. In addition no method of evaporation by high voltage bombardment, such as they used, had been developed and the heat generated in melting and evaporating small lumps of Be from a tungsten filament seriously endangered the steel radiation shield and nickel supporting rods, on two occasions entirely fusing them.

Attempts to make evaporated Cu adhere to the Cu anode which could not be outgassed also were unsuccessful, the evaporated film peeling off under electron bombardment. Finally a Cu strip was mounted in a completely separate vacuum chamber, and heated to redness electrically. It was found that a beryllium coat would adhere when the copper was so prepared, although the addition of a removable mica screen to catch the first "dirty" layer of Be was necessary for really clean coatings. The evaporated layers produced in this way were rather thin; less than $.001 \text{ gm/cm}^2$. However any attempts at heavy deposits resulted in peeling and flaking off of the entire coating. One target was produced in this manner and soldered to the anode. In spite of the ra-

ther heavy overlay of barium from the emitter, a weak BeK line appeared on the plate along with a stronger Ba line-- a testimony of the intensity of the K radiation of Be.

The only other attempt at using metal films for the targets was by nickel-plating the copper anode with a layer about .0005" thick. This anode was bombarded to redness. On the plane surface the nickel was smooth and adherent; on the remainder, where the surface had not been so carefully cleaned, minute blisters (gas?) were formed over the surface. Difficulties with evaporation and gas pressure prevented a run with this target.

c). Alignment:

When target and emitter have been properly prepared for use, it is necessary to align them accurately with respect to slit and grating. The steps of this process occur in the following order: a) A square-ended metallic pointer is inserted in the porcelain cone, normally (see figure 3) used for the cathode, and waxed in place. b). A 1 mm vertical slit is placed at the normal position of the central image of the grating. c). A broad source of light is placed behind this slit somewhere on the Rowland arc, in such a position that the shadow of both the pointer and the horizontal slit can be observed on a ground glass when looking along the porcelain tube which normally holds the anode. d). The pointer is adjusted so that the shadow of

its square top falls in the center of the rectangle of light which represents the slit, thus:

Because the image is enlarged the pointer may be set thus to about $1/10$ mm.

e). The anode is inserted, taking care that the freshly polished target surface is not scratched against the pointer, and adjusted so that it just touches the tip of the pointer. Contact may be determined electrically with headphones and a source of low voltage A.C. This method sets the anode against the pointer to within $1/20$ mm. In fact, mere flexure of the anode assembly due to outside forces is sufficient to make or break the circuit.

The anode is usually adjusted so that a definite scratch on its side surface is opposite the pointer, then the pointer is removed and replaced by the emitter, which is adjusted to have the same slope as the target surface and to be centered on the aforementioned scratch. The emitter was normally operated about 2 to 3 mm away from the target, the farther away (without current limitation by space charge) the better.

d). Outgassing

Since pressures of less than 10^{-6} during operation were prerequisite for satisfactory operation of the oxide emitters, it was essential that all residual gases be removed from metal parts before beginning activation of the easily poisoned emitter. Naturally the target, subject to intense electron bombardment and dissipating as high as three hundred watts, received first attention. A special bombarding filament, consisting of 15 turns of $8\frac{1}{2}$ mil tungsten in a 2 mm helix, was mounted in a Ni radiation shield beside the emitter. When heated with about 4 amperes it would yield emissions of 20 to 30 mils, at 2000 volts, which would suffice after 2 or 3 minutes time to heat the copper target to redness. Naturally water cooling was disconnected during bombardment. The silver-solder joint between Ni supporting tube and copper target showed no signs of softening or leaking, although the target was accidentally heated to a rather bright red at times. The thermal conductivity of the Ni was sufficiently poor that very little heat was conducted to the grease joint, and no special cooling of this cone was necessary if bombardment was restricted to a very few minutes duration.

This bombardment, as well as the initial activation of the emitter, was carried out on the back or curved surface of the target, in order to keep the plane face as

clean and free from Ba and tungsten as possible. After they were completed the target was rotated 180° in its brass ground joint, which was lubricated with the special low vapor pressure Apiezon L grease. Pressure changes from 5×10^{-7} to 2.5×10^{-6} were observable at the first heating of the bombarding filament and again at the first application of the bombarding potential. About 15 minutes was required for the pressure to return to normal after the cessation of these heating and bombarding activities. No pressure change was observed upon rotation of ground joint, providing this was done carefully. The emitter gave off considerable gas upon heating, both from decomposition of the carbonates and diffusion out from the box itself. Heating the emitter boxes to redness in H_2 before coating was tried in several cases, but so many other factors enter in the activation process that it was not proved that saturation with the H_2 was useful.

The ionization gauge was provided with a circuit so that each element could be outgassed. Heating the collector with 8 amps for 30 seconds and the grid with 6 amps for 30 seconds provided sufficient outgassing. Higher or longer currents than these would be liable to warp the elements or crack the seals. As a matter of fact leaks were found in both collector and grid glass-tungsten seals even before the gauge was operated, and had to be stopped with

glyptal lacquer. The difference in apparent pressure before and after outgassing was slight, not greater than 10% at 10^{-6} mm Hg, but might become more important at lower pressures.

e). Activation

The activation of the emitter was usually not begun until the pressure in the x-ray tube was considerably less than 10^{-6} , say 5 to 7×10^{-7} , because considerable gas was always evolved during activation, and it was desirable to keep the pressure near 10^{-6} at all times. The "breakdown" or decomposition of the original carbonates into CO_2 and oxides, was accomplished by heating the emitter to a bright red or orange (this is about 1200° K or 5 amps heater current) for three to five minutes in the absence of any electrical field. It is doubtful if this amount of heating completely degasses the emitter, but more prolonged heating occasionally tended to produce heavy evaporation of barium, in spite of the statement of Reimann⁴¹ that barium does not evaporate from an unactivated filament below 1250° K. Previous "soaking" of the emitter box in H_2 and later release of this reducing agent in contact with BaO may partially explain this anomalous evaporation.

When the pressure had returned to equilibrium value after the "breakdown" was completed, a potential of 200 to 500 volts was gradually applied, the box being held at a dull red heat (about 950° K or 3.5 amps heater current).

If at any time during this process emission set in, as indicated by currents of 3 to 5 M.A. in the high voltage circuit and a slight bluish surface glow (usually local) on the target, further heating was stopped and the emission allowed to grow spontaneously. When the emission had reached a value of about 30 M.A. the temperature was gradually reduced to about 1000° K (3.65 amps heater current) and the voltage simultaneously increased in such a way as to maintain at least 30 M.A. emission.

Usually this rather idealized procedure could not be carried through, and it was necessary to overheat to 4.5 or 5.0 amperes (1250° K) heating current, and then raise the voltage from 500 to about 1500 volts or even the maximum of 2000 volts. Usually emission could then be started, although under these conditions it built up very rapidly and care had to be taken to reduce the voltage as soon as possible. In general, it was necessary to draw a current of 80 to 100 mils at some fairly high emitter temperature for several minutes before the activation had spread so that emission could be maintained at 20 or 30 mils at 1000° K.

Often the possible currents were limited to 10 M.A. or less at 1000° K, even with 2000 volts E.M.F., usually because of gasey target conditions. It must also be borne in mind that in the activation process BaO is converted to metallic Ba at the surface of the coating, and in the resulting liberation of O_2 the filament may temporarily "poison"

itself. It has been shown by Reiman⁴² that when two oxide emitters are mounted together it is possible for one to "poison" or deactivate the other. Consequently it is desirable to carry out activation slowly, so that too high gas pressures are not built up.

Any time that the potentials used were greater than 1000 volts, there was danger of "bursts" or sudden surges of current due to arcing between emitter and anode, with consequent evaporation, fusing and disintegration of part of the emitter surface. They were usually preceded by the appearance of small glowing specks of coating material adhering to the target and sometimes brilliantly incandescent. These specks were not always followed by bursts, but the burst rarely occurred unless preceded by glowing particles, although it is true that the time elapsing between the appearance of the specks and the burst was often only a second or two.

These "specks" and "bursts" which occur during activation are most probably when the voltage and temperature are simultaneously high, as then the efflux of gas is greatest and the coating adhesion is poorest. They are especially prevalent at the beginning of activation, until all parts have had time to outgas and reach equilibrium. Another time that they have been noticed is when the voltage is high and the cathode temperature very low. It is possible

that at low temperatures the I^2R heat developed in the coating is sufficient to cause strong local heating and emission, which builds up cyclically and causes a small eruptive arc at one point. Coatings are sometimes made with admixtures of powdered metal⁴³ to avoid this effect, which is due to the rapid (exponential⁴⁴) variation with temperature of the coating resistance.

It was found experimentally that when an activated emitter (in this particular case the smaller of the two available boxes) was heated by 3.6 amperes (about 850°K) for twenty minutes no visible coat of barium was formed on the polished copper anode, but that when 4.0 amperes (about 1020°K) were used a definitely opaque coating was formed after ten minutes. Both tests were made while no emission was being drawn. According to Reimann⁴⁵ Ba is not evaporated from a surface at temperatures less than 800°K , but the normal operating temperature of his oxide cathodes is 1020°K , which in our apparatus would produce definite evaporation. On the other hand Skinner and O'Bryan⁴⁶ state, discussing effects of evaporation, that "it was quite possible by paying attention to the vacuum to avoid the barium lines completely." In the same article they state that currents of 400 M.A. were used in making exposures for Be, presumably with no appreciable evaporation. In a private communication from Mr. O'Bryan an approximatley to scale sketch of his emitter was included which would indicate that the total

emitting area could not exceed about $2\frac{1}{2}$ sq. cms., as compared to about 1 sq. cm. in our own. In view of the preceding statements, it is hard to understand why our own emitters would give only about 20 M.A. at 800° K while those of Skinner and O'Bryan apparently gave 400 M.A. at the same temperature. Perhaps our pressure measurements are erroneously calibrated, or the filament is being "poisoned" by one of a number of causes which will be discussed presently. In any event it would be of interest in the future to make a direct calibration of the ionization gauge with a McLeod gauge, and a careful redetermination of the actual upper limit of emitter temperatures at which evaporation does not take place.

A very interesting type of spurious "non-thermionic" emission could be obtained at very low emitter box temperatures, providing the pressure was high, i.e., somewhere in the range 10^{-4} to 10^{-5} . After this emission was once established, it was very insensitive to box temperature, in fact it would maintain itself even when the box was at barely visible red heat (720° K). However, it was very sensitive to voltage, and above a certain critical voltage the emission very quickly went beyond control and arced. The emission was not stable, but suddenly "popped" out when voltage or temperature went below certain critical values, and could not be re-established without greatly exceeding these values, when it as suddenly began again.

Two characteristic features of this type emission were the definite and visible cooling of the emitter box (dull red to black) when emission ceased, and the blue columnar space glow between electrodes. Examination of this glow spectroscopically revealed strong red and blue lines, which are also present in the spectrum of barium vapor, but no bands characteristic of air. However the intensity was too low for definite identification to be made. When the electrode spacing was increased beyond five millimeters, emission could not be established.

The writer suggests as a possible mechanism for this emission the following process: (a) The overheated cathode evaporates barium upon the anode. (b) Emitted electrons from the cathode sputter barium ions loose. (c) These 2000 volt barium ions bombard the cathode, heating it and thereby increasing both emission and further evaporation of barium. (d) The process continues in cyclic fashion, building up until limited by the rate of transfer of barium or reduction of applied potential. It is difficult to see how the air molecules alone could be responsible for the observed behaviour, because of the "poisoning" effect of the oxygen, although they undoubtedly play a role. The voltage sensitivity of the current, and the heating of the cathode, point strongly to some ionization process.

Poisoning, or deactivation of the emitter, can

occur from a number of cause, chief among which is exposure to oxygen or water vapor. Since the active portion of an emitter is a monomolecular layer of metal, it is easy to see how very small amounts of oxygen would suffice. Blanketing of this layer with some neutral substance such as evaporated nickel would likewise reduce emission, as was discussed in the section on bulk metal targets. Impurities in the base metal and overheating are also possible sources of trouble, and are discussed⁴⁷ by various workers, as well as methods of reactivation⁴⁸ involving sputtering away of the contaminated surface layer by argon or hydrogen. In the only attempt by the writer to use hydrogen for reactivation, the emitter box was heated, consequently all the oxide reduced to metallic barium, and moreover barium was diffused throughout the x-ray tube. Evidently these methods apply to cathodes only when cold. In an emitter which has been overheated too long, the more volatile barium has evaporated, leaving a preponderance of strontium compounds, and the original activity cannot be restored.

f). Magnetic Shutter

The shutter actually used has been sufficiently described on page 9 and in figure 5. It should be mentioned that two other types were tried. The first, and simplest, in which an iron disc with a hole was pulled back and forth

in front of the slit, did not work because induction effects from the adjacent iron spectrograph cone weakened the field of the external magnet. A modification of this in which a piece of iron was set in an aluminum vane, designed to give greater effective torque, was inoperative for the same reason. The first model of the final cylindrical type had a block of iron fastened to one side of the cylinder instead of diametrically, consequently the external magnet exerted a net translational force as well as a torque, and the resulting friction rendered the device unreliable. The present model could be rendered more positive in action by decreasing the external air gap in the magnetic circuit.

g). Exposure of Plates

The amount of exposure was considered proportional to the product of the emission current by the time of exposure. Skinner and O'Bryan report adequate plate densities of Be K with 100 M.A. hours exposure. The writer's best plate (No. 14) of the Ba O - N band was exposed for 300 M.A. hours. This method of estimating exposure neglects such obviously important factors as slight inaccuracies in target alignment, slit width, amount of surface impurity, exact voltage of bombarding electrons (occasionally it was necessary to use potentials slightly below 2000 V for the sake of stability) effect of the unfiltered wave form on efficacy of excitation, and effect of change in electrode spacing,

which would of course change the current density. In fact plate No. 14 mentioned above was more than three times as dense as other plates which had 30% to 50% more exposure. In the case of transitions of low relative probability, such as the M N of nickel, it might be necessary to greatly increase the exposure, say to 1000 M.A. hours on a clean target, before the line would appear.

Usually if bombarding currents were greater than 50 to 70 mils, they tended to grow spontaneously and the x-ray tube required constant attendance and adjustment. Currents less than 40-50 mils would ordinarily remain stable or decline slightly over a period of 3 to 5 hours. It was necessary of course to renew the liquid air on the charcoal trap at similar intervals, if the pressure was to be kept at optimum values.

Due to the irregularity of the Schumann plates there were usually a considerable number of spots and dark areas occurring at random positions. 4" x 10" plates were cut into 1" x 10" strips, the two center strips being used when greater freedom from irregularity was imperative. They require careful development, as they fog easily. In one case (plate #11) development in warm overconcentrated solutions blackened the plate to the point of eliminating all traces of exposure. Best results were obtained by developing for $1\frac{1}{2}$ minutes at $^{\circ}\text{C}$ in Eastman's standard D-11

formula which had been diluted with two volumes of water. Wavelengths on these plates were determined from the geometry of the Rowland arc and the known grating spacing, since great accuracy was not essential in a preliminary survey. The copper anode however was provided with openings to clamp an aluminum electrode, with which spark comparison lines could be produced when necessary.

h). Hunting Leaks

When the entire system was properly sealed and vacuum tight, the combined action of mercury and rotary pumps would reduce the pressure to less than 10 cm. in 10 minutes, and to a "black" vacuum (less than 10^{-2} cm) in about 45 minutes. It was then necessary to pump for 12 or 15 hours longer to remove absorbed gases and vapors sufficiently to lower the pressure to less than 10^{-6} in the x-ray tube, the charcoal trap being cooled meanwhile. Even when the charcoal was being baked out to 460° C or higher preparatory to a run, the pressure with Hg pumps in operation could be kept below 10^{-2} mm.

When the pressure did not fall at the above rate, a leak was suspected. A small leak in the x-ray tube could be traced with the help of the ionization gauge, which responds immediately to the change in pressure when the leak is plugged. Larger leaks in the x-ray tube may be

checked by the emission of the ion gauge, which at the recommended voltages (see figure) emits 5 mils at a reading of 1.10 amps on the ammeter if the pressure is 5×10^{-6} and requires 1.15 amps or more if the pressure is 10^{-5} . Leaks in the spectrograph are best located by closing the large stop-cock (let pumps run) and observing the Pirani gauge over a period of 3 to 12 hours. When the spectrograph is tight it should remain below the "black" vacuum point (470 ohms on Pirani) for several hours at least. The maximum reading on the Pirani is about 525 4 ohms. In case of a stubborn leak in the x-ray tube system, it is possible to remove the charcoal trap and immerse the suspected parts in a CO_2 bath, when the discharge tube will show a characteristic whitish color if appreciable CO_2 leaks into the system. The writer finds this method rather uncertain, but it might possibly be made more sensitive by inserting a discharge tube on the outlet side of the mercury pumps. "Plasticene," a specially refined modelling clay, has been suggested as a possible convenient substance for covering suspected leaks.

The most frequent sources of leaks are in the beeswax-rosin joints, particularly those to the mercury pumping line and the spectrograph. Other places where leaks have been found are the brass to brass ground joint, glass stop cocks, (degreasing) ionization gauge, tungsten seals, glassware cracks due to strains near the brass to

glass pump connections and large stop cocks, and in the
Picein wax joints. The spectrograph rubber gasket also merits
attention in this respect. Good sealing wax joints have
never given trouble.

Barium and Strontium
Plate #14

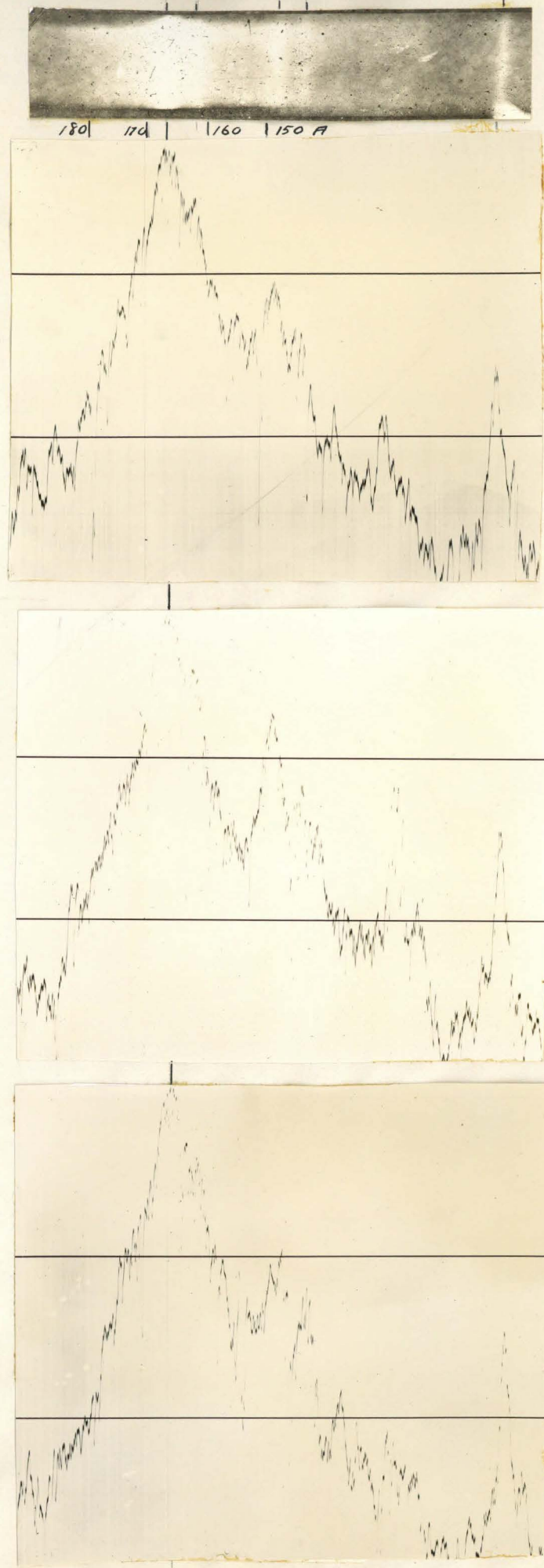


Figure 14

Barium - Plate #19



180 170 160 150 M

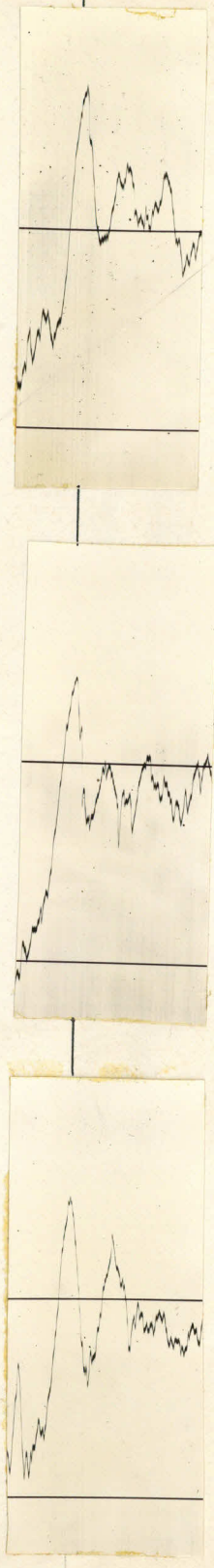


Figure 15

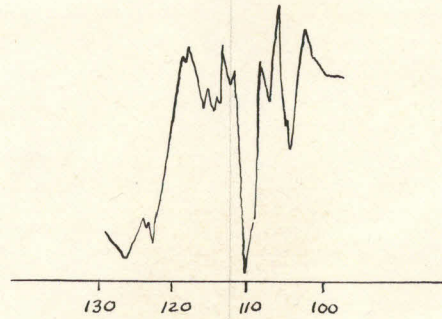
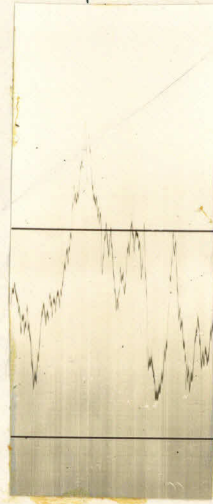
Be K

Barium and
Beryllium - Plate #12



167 A

110 A 100 A



Faust P.R. 36, 171, 1930

Figure 16

V. RESULTS AND CONCLUSIONS

X-ray lines in the 40-400 A° range have actually been photographed, and the technique and equipment for producing the required vacua and sources of electrons developed. It is believed by the writer that the possibility of producing low pressures and high emission currents with a Siegbahn type metal x-ray tube has been shown. There still remains to increase the reliability of vacuum production and the efficiency of the emitters. While oxide emitters have been highly developed commercially, most of this information is not made public: to improve their efficiency will be no mean task.

Six plates were obtained which showed the barium ON line, of which the most dense showed two barium and two strontium lines. One plate each was obtained of Be and C as well. Some of these plates are shown in figures 14-16. Figure 14 shows three photometerings of the heavy Ba and Sr lines on plate #14, while figure 15 shows three successive sections of the Ba line on plate #19. Finally figure 16 shows a trace of the faint Be line on plate #12. The Ba lines show no traces of asymmetry which are significant; in this respect they confirm the work of O'Bryan and Skinner. However, the irregularity of the Schumann plates is great, the resolving power is low (2 - 3 A°) and the purity of the

surface uncertain, so these curves cannot be regarded too seriously. The Be line curve #6 (d) shows much structure, as did that of Faust⁴⁹, but its structure shows no particularly definite correlation with that of Faust's line and disagrees completely with that of Skinner and O'Bryan, as would be expected from the evident contamination of the surface.

The negative results obtained in the case of Cu, Ni and KBr are believed adequately explained by evaporation and pressure difficulties, although the Cu and Ni lines may be inherently weak, as mentioned by Skinner⁵⁰. Br has been successfully photographed by Siegbahn⁵¹ in the form of Rb Br, which presumably is an insulator, but his method of producing targets is not described.

The indicated steps in continuing work on this problem will probably include the following: a) consistent control of pressure, b) increase in emitter efficiency, c) survey spectra of the (contaminated) conductors of the first long period, d) development of evaporation technique for these conductors, e) spectra of the pure metals, and f) spectra of insulators and compounds.

VI. THEORETICAL DISCUSSION

a). Physical Picture

1). Energy Levels:

Since the spectra from solid metals consist of broad lines, while the same metals when in the form of isolated atoms (spark spectra) give sharp lines, the inference is clear that bring^{-ing} atoms together in the solid crystalline state in some way spreads the number of available energy levels into a virtual continuum. Classically this is analogous to the multiplication of frequencies (normal modes) upon coupling of identical harmonic oscillators. From the wave mechanical point of view, the crystal may be regarded as a single system which would have as many ways of realizing a given energy as there were atoms in the crystal (say N), in other words which would be N -fold degenerate, if it were not for the separation of its energy levels into bands. These bands actually consist of a large number of discrete levels, and as calculations will later show, there is one level for each atom in the crystal, so that for practical purposes the bands are continuous. According to Slater⁵² this may also be regarded in the light of Heisenberg's uncertainty principle. Since the lifetime of an electron in any one state is finite (due to its probability of transference from atom to atom in a metallic lattice) then its conjugate energy cannot be determined accurately, according

to the well known relation $\Delta E \cdot \Delta \tau \approx h$. The actual emergence of these bands in the calculation of solutions of the Schrodinger equation is perhaps more convincing than the preceding generalizations.

The magnitude of the broadening of a given atomic energy level depends on the degree to which it is perturbed by the presence of other atoms, hence low-lying levels such as K and L are but little broadened in heavy atoms. In atoms for which the L level is the exterior one such as Li and Be considerable broadening, of the order of 10 e V, may occur. Since each level is split into N parts, this means that the density of states in the interior bands is very great. On the other hand two adjacent exterior bands may be spread out until they overlap, as is the case with the L_{III} and L_{IIII} levels of Mg. Such a situation will reveal itself in the form of the emission bands beginning on these levels. Specific examples are given by Frohlich⁵³.

On the basis of these bands it now becomes possible to distinguish between conductors and insulators. In the words of Skinner and O'Bryan⁵⁴, "A good conductor is a substance with a large number of unoccupied levels within a small energy range above the highest occupied level." This means that an electron may easily absorb momentum from an externally applied field, which is the phenomenon of conduction.

If, however, the band is completely occupied with electrons, and no other unoccupied band is adjacent or overlapping to it, then the electrons may not absorb momentum in very small amounts, since they may not increase their energies by small amounts, and no current flows.

~~Semi~~-conductors are special cases of conductors in which the density of unoccupied levels is so small that only a small fraction of the available electrons may transfer to them. The way in which these various band configurations affect emission spectra will now be discussed.

2). Emission of Radiation:

The typical x-ray emission line results from the jump of an electron from an outer occupied level of the atom to one of the inner levels from which the tenant electron has recently been ejected by a photon. The typical optical line occurs when an electron which has been excited to a virtual level outside the atom falls back to its normal position in the valence shell. The distinction between optical and x-ray spectra is one of degree, and discussions have been given of intermediate⁵⁴ types.

When an electron falls from one of the energy "bands" of a crystalline target to an inner level, the wavelength emitted may have any of a range of values, depending on the width of the band. This produces a broad line.

For radiation of about 1 \AA° (12,000 e V.) the 10 e V width of the band produces no appreciable broadening of the line. However for "soft" x-rays of 100 \AA° or so the broadening of 10 e V results in a wavelength spread of 10 \AA° or so, and with the resolving power of the spectrograph previously described ($1 \text{ \AA}^\circ/\text{mm}$) structural detail is easily measurable. This is the reason why soft x-ray investigations are of superior worth in examining conduction properties, in spite of the great experimental difficulties involved.

The actual contour of the line will depend both on the density of levels and the probability of transition. That is

$$I_E = n_E f_E \quad E < E_{max}$$

where I_E is the intensity of radiation of energy E , f_E is the number of transitions per unit time to some level (supposed sharp), and n_E is the number of levels per unit energy range. According to Frolich⁵⁶ f_E is a smooth slowly varying function of E . Houston⁵⁷ calculated f_E for BeK as $\sim f$, using the free electron model, while Jones, Mott and Skinner⁵⁸ calculated f_E for both BeK and Mg $L_{II,III}$, using the method of Bloch and Brillouin, to be described later. The actual calculation of f_E is somewhat involved and requires knowledge of wave functions appropriate to the particular substance. Frohlich⁵⁹ has given some details

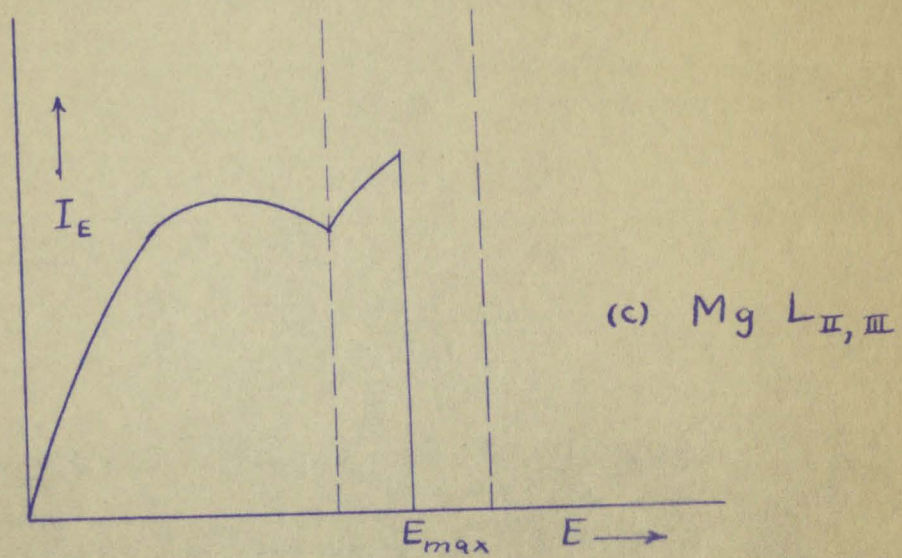
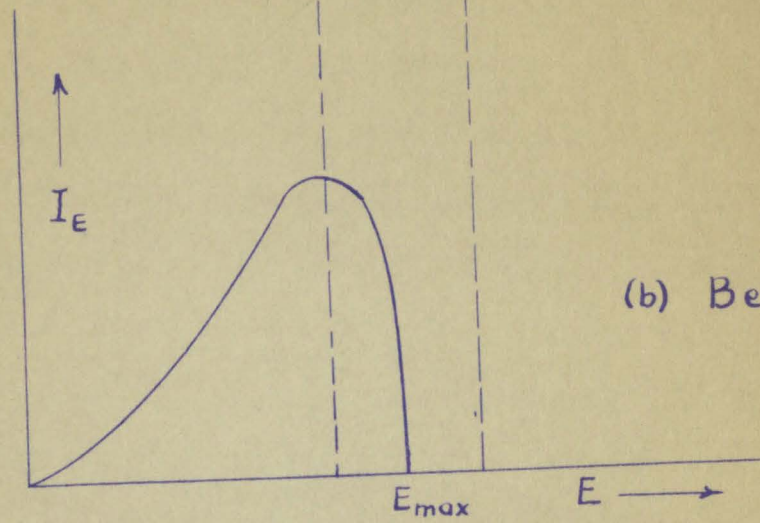
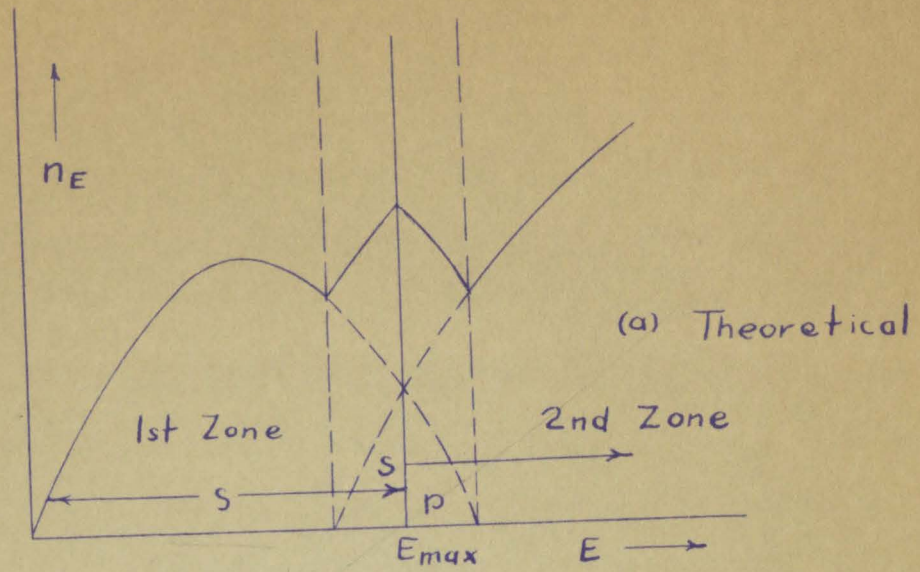


Figure 17

of such a calculation, starting from the fundamental definition⁶⁰ that transition probability per unit time is proportional to the square of the matrix component of the interaction energy between the field and the electron. That component is used whose initial indices specify the initial state and whose final indices specify the final state.

Jones, Mott and Skinner have calculated the density of levels for the first two Brillouin zones of a typical metallic lattice, and applied the result to the special cases of *BeK* and *Mg L_{II,III}*. The result of these calculations is shown qualitatively in figure 17.

It can be seen that for Be the curve falls rapidly after the maximum, but without a sharp edge. This is due to the fact that n_E is already decreasing (figure 17 a) before the available electrons have been exhausted at E_{max} . Although the second zone apparently overlaps the E_{max} line, electrons in it are s electrons, and hence cannot make transitions to the K level and do not contribute to I_E . Evidently we must consider, however, that the ordinary selection rules are somehow invalidated for solid Be, and that the outer electrons, in the first zone, (ordinary s electrons) must have finite transition probability to the K level, if the existence of a line is to be accounted for.

On the other hand, we may explain the Mg line by saying that electrons from both zones may contribute to *Mg L_{II,III}*,* since the two zones now contain "s" electrons.

*See Condon & Shortley, p. 317, for correspondence between optical & x-ray notation.

It is apparent from the diagram that before E_{\max} is reached, and while n_E is decreasing, the introduction of electrons from the second zone causes the curve to start sharply upward again. In their paper⁶⁰ Jones, Mott & Skinner discuss these curves in detail, including the effects of variations in f_E .

It is to be noted that the shape of the B_a line, given in experimental results, figure 14, is characteristic of an insulator, in that it is narrow and symmetrical. This is to be expected from the fact that the line represents an $O \rightarrow N$ transition, and the O band is completely filled and separated by a definite gap from the conduction levels, although the O level itself is not very narrow.

b). Mathematical Treatment

1). Self-Consistent Fields:

Schrodinger's equation if applied rigorously to the many-body problem of the motion of all the electrons in a crystal would lead to a wave equation of the form⁶¹

$$\textcircled{1} \quad (H-E)\Psi = \left[\frac{\hbar^2}{8\pi^2 m} \sum_i \Delta_i + \sum_{i>k} G_{ik} + \sum_{\alpha, i} V_{\alpha i} - E \right] \Psi = 0$$

$i, k = \text{electrons}, \quad \alpha, \beta = \text{ions} \quad G_{ik} = \frac{e^2}{r_{ik}}$

$N = \text{total no. atoms} \quad \Psi = \Psi(x_1, y_1, z_1, \dots, x_N, y_N, z_N) \text{ complete wave fn.}$

This equation is too difficult to solve as it stands so it is ordinarily broken up into separate equations, one for each electron, as follows:

$$\textcircled{2} \quad \left[-\frac{\hbar^2}{8\pi^2m} \Delta_i + \mathcal{U}_i(x_i, y_i, z_i) - E_i(a_i, b_i, c_i) \right] \Psi_i = 0$$

Where a_i, b_i, c_i are quantum numbers characteristic of the energy of the i th electron, and \mathcal{U}_i is the potential of the i th electron in the field of the nuclei and all the other electrons. \mathcal{U}_i is then of the form

$$\textcircled{3} \quad \mathcal{U}_i = \sum_{\alpha} V_{\alpha i} + \sum_k \int G_{ik} \psi(a_k, \dots, x_k, \dots) \psi^*(a_k, \dots, x_k, \dots) d\tau_k$$

The integral cannot be evaluated without knowledge of the wave function, which is the unknown variable. Consequently a zero approximation is taken for \mathcal{U}_i and substituted in (2), which is then solved for the 1st approx. wave function Ψ_i' , which leads in (3) to a corrected value (first approximation) of \mathcal{U}_i to use again in (2). When this cyclic process leads to the same function Ψ_i as a solution of (2) as was used in the preceding calculation of \mathcal{U}_i in (3) the equation is solved. This method is known as the method of self consistent fields, and is due to Hartree.

2). Tightly Bound Model:

To actually solve (2) above it is necessary to take special cases which invoke the properties of the system considered. The periodicity of a crystal is of great assistance in finding a form in which to write \mathcal{U}_i , the unknown function necessary to the solution of (2). Suppose in addition to three dimensional periodicity, we assume the elec-

tron to be one of "low" energy (strongly bound). Then solutions of (2) can be found as perturbations⁶² of the solution for the isolated atom. The potential will have the property

④
$$U_{g_1, g_2, g_3}(xyz) = U(x - g_1 a, y - g_2 b, z - g_3 c)$$

Where g_i are integers which locate a particular nucleus of the crystal lattice. The notation $g_1 g_2 g_3$ follows Bloch⁶³ whose method is here outlined. The atomic wave function $\psi_{g_1 g_2 g_3}$ is used as a zero order approximation, and the energy written $E = E_0 + \epsilon$ where ϵ is a small perturbation term. Carrying through this approximation leads to the perturbed set of energies

⑤
$$E = E_0 + \alpha - 2\beta \left(\cos \frac{2\pi k}{G_1} + \cos \frac{2\pi l}{G_2} + \cos \frac{2\pi m}{G_3} \right)$$

Where G_i are the maximum values of g_i and k, l, m are integers. α is a constant addition to the energy due to the presence of neighboring nuclei, while β , the "exchange" integral, is a measure of the interference of the electron's ψ wave with those of all the other electrons. Its magnitude is small in the case of low lying electrons, which show but little coupling with electrons in other atoms. An excellent illustrative example of the exchange (Austausch) integral is given by Frohlich, p. 33.

3). Loosely Bound Model:

In this model the electron is thought of as almost free, moving through a field in which the perturbations due to atoms are small. Since the potential is periodic, it is convenient to expand in a Fourier series. Returning to the notation of reference (10) and equation (1) let us set

$$(6) \quad U_i = \sum_{\alpha\beta\gamma} P_{\alpha\beta\gamma} e^{\frac{2\pi i}{d}(\alpha x_i + \beta y_i + \gamma z_i)}$$

where d = edge of lattice cube
 α, β, γ = integers

$$P_{\alpha\beta\gamma} = P_{-\alpha, -\beta, -\gamma}^*$$

Bloch⁶³ and Brillouin⁶¹ have shown that each state of an electron in a metal is denoted by a vector \bar{a}_i (called \bar{k}_i in later work). The direction of \bar{a}_i is the direction of motion of the electron, and $\frac{2\pi}{|a_i|}$ is its de Broglie wave-length. Bloch has shown (ref. cit.) that the wave function for each individual electron takes the form

$$(7) \quad \Psi(a_i, b_i, c_i; x_i, y_i, z_i) = A(a_i, \dots, x_i, \dots) e^{2\pi i(\bar{a}_i \cdot \bar{r}_i)}$$

where $A(a, x)$ is periodic with the period of the lattice. The energy is a function of \bar{a}_i ; for the values of a_i, b_i, c_i corres-

ponding to Bragg reflections of the ψ waves from the lattice points of the crystal, a discontinuity in the energy occurs. Thus the states of an electron in the metallic lattice may be divided into zones in \bar{a}_i space, called Brillouin zones, separated by planes (in \bar{a}_i space) across which the energy is discontinuous. Since A in (7) is periodic in the lattice spacing, we may also expand it as follows: $(\alpha_i, \beta_i, \gamma_i, \text{integers})$

$$(8) \quad A(a_i; x_i) = \sum_{\alpha_i, \beta_i, \gamma_i} A_{\alpha_i, \beta_i, \gamma_i}(a_i, b_i, c_i) e^{\frac{2\pi i}{d}(\alpha_i x + \beta_i y + \gamma_i z)}$$

Substituting (8) in (7) and the result of this combination, along with potential expansion (6), back into the original wave equation (2), and equating coefficients of exponential terms, there results a relation between the ψ_i coefficients and the U_i coefficients

$$(9) \quad \frac{\hbar^2}{2m} \left[\left(a_i + \frac{\alpha_i}{d} \right)^2 + \left(b_i + \frac{\beta_i}{d} \right)^2 + \left(c_i + \frac{\gamma_i}{d} \right)^2 \right] A_{\alpha_i, \beta_i, \gamma_i} - E_i A_{\alpha_i, \beta_i, \gamma_i} + \sum_{\alpha', \beta', \gamma'} P_{\alpha' \beta' \gamma'} A_{\alpha - \alpha', \beta - \beta', \gamma - \gamma'} = 0$$

If $U_i(\psi_i)$ is nearly constant, we may choose $P_{000} = 0$ and the $P_{\alpha\beta\gamma}$ will be small. This implies that the electrons are almost free, and that the amplitude of ψ is almost constant; hence

$$A_{000} \gg A_{\alpha, \beta, \gamma}$$

The normalization of ψ_i tells us in this case that

$$A_{000} = \frac{1}{\sqrt{V}}$$

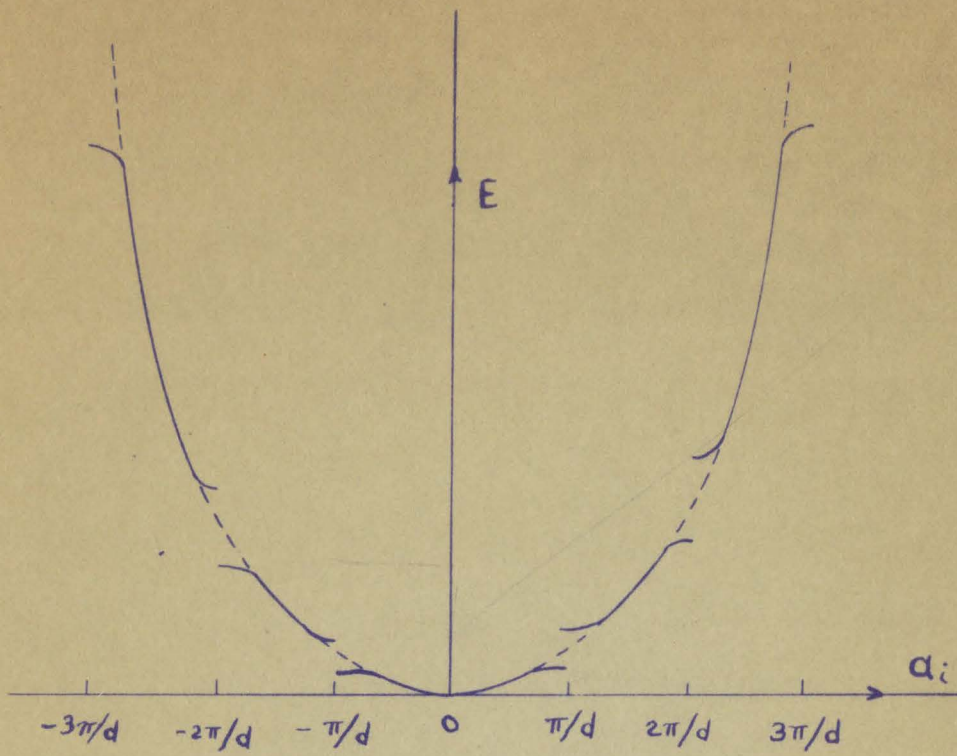


Figure 18

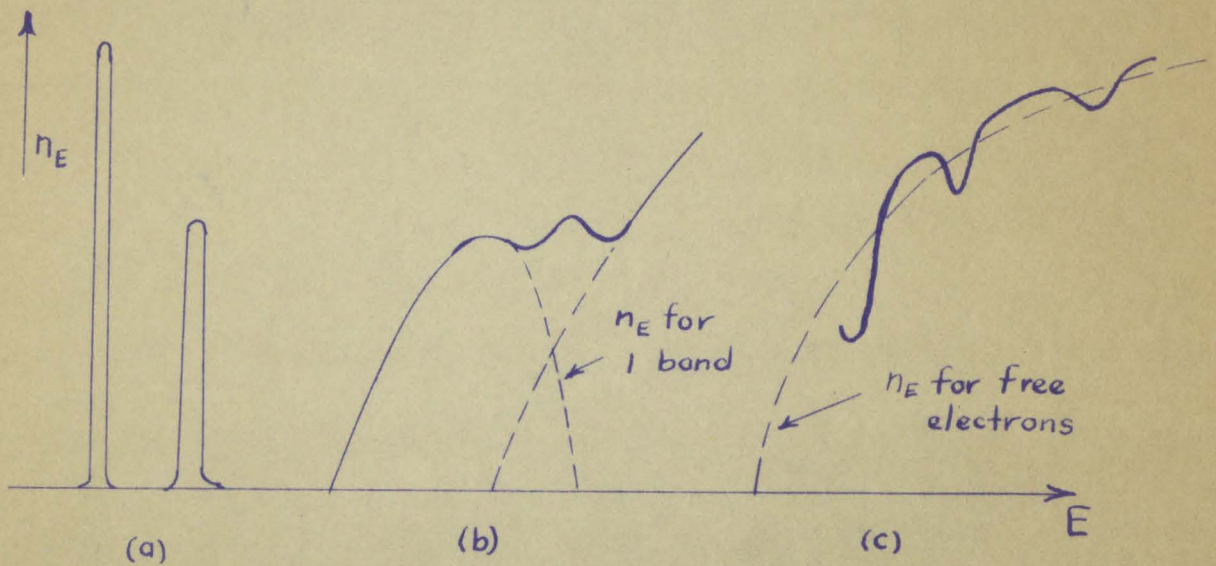


Figure 19

The set of equations (9) for the case $\alpha_i = \beta_i = \gamma_i = 0$ gives

$$1) \quad E_i = \frac{\hbar^2}{2m} (a_i^2 + b_i^2 + c_i^2)$$

as an approximation to the energy for small values of \bar{a}_i . If this energy is used in (9) to calculate a second approximation, there results

$$2) \quad H_{\alpha, \beta, \gamma} = -\frac{2m}{\hbar^2} H_{000} \frac{P_{\alpha, \beta, \gamma}}{2 \left(\frac{a_i d_i}{d} + \frac{b_i \beta_i}{d} + \frac{c_i \gamma_i}{d} \right) + \frac{\alpha_i^2 + \beta_i^2 + \gamma_i^2}{d^2}}$$

The $H_{\alpha, \beta, \gamma}$ are small unless the denominator approaches zero, at which points perturbations to the "free electron" energy given by (10) occur. The denominator approaches zero, for example, when

$$3) \quad a_i = \frac{1}{2d} \pm \frac{2md}{\hbar^2} \eta \quad \eta \rightarrow 0 \text{ (parameter)}$$

When (12) is substituted in the set (9) and we take the special case for which $\alpha_i, \beta_i, \gamma_i = 0, 0, \pm 1$ and $b_i = c_i = 0$, there results an expression for the energy E in the vicinity of the discontinuity as follows

$$3) \quad E = P_{000} + \frac{\hbar^2}{2m} \left(\frac{1}{4d^2} + \frac{4m^2 d^2}{\hbar^4} \eta^2 + b^2 + c^2 \right) \pm \sqrt{\eta^2 + |P_{100}|^2}$$

A plot of energy against a_i for the one-dimensional case is shown in figure 18, showing discontinuities in E .

A general calculation of the energy can be obtained formally, after the ψ_i & $\bar{\psi}_i$ are known, from the ordinary quantum-

mechanical method as follows:

$$\bar{E}_i = \int_V \psi_i^* E_i \psi_i d\tau = \int_V \psi_i^* H_i \psi_i d\tau = \int_V \psi_i^* \nabla_i \cdot \psi_i d\tau - \frac{\hbar^2}{8\pi^2 m} \int_V \psi_i^* \Delta \psi_i d\tau$$

4). Intermediate Energies:

Frolich⁶⁴ discusses calculation of energy levels for cases intermediate between the loosely and tightly bound models. The method used is a combination of these two, the electron being treated as tightly bound when it is within a certain sphere of critical radius about the nucleus (Atomrumpfe) and as loosely bound at other points. The general results are shown in figure 19, where energy level densities are shown for a) low lying electrons, b) intermediate electrons, and c) almost free electrons.

These curves have already⁵⁸ been successfully applied to interpret the results⁵⁴ of experimental work. Frolich remarks⁶⁵, "Durch diese Experimente wird unsere Theorie der Leiter und Nichtleiter sehr schön bestätigt."

VII. ACKNOWLEDGMENTS

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