A FIELD EMISSION

ION SOURCE

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SCOPE AND CONTENTS:

　　　　The construction of a field emission ion source and its
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INTRODUCTION

History

Field emission is generally concerned with the emission of electrons from solid surfaces under the influence of high electric fields, fields of the order of volts per angstrom unit. Atoms also can become ionised in fields of this magnitude, which is the basis of the field emission ion source.

Field emission of electrons has been extensively studied since the 1920's. The first attempt to explain the emission of electrons from cold surfaces was made by Schottky[1] who interpreted it as a result of the lowering of the potential barrier at the metal surface by a combination of the applied field and the electron image potential of the barrier (see figure 1A). The electron image potential represents the attraction of the electron to the charge it induces on the statistically neutral metal surface. The field required for the above explanation was some ten to a hundred times greater than that which was observed to be necessary, so it was considered that emission came from minute protrusions on the surface where the field was much enhanced. Schottky's theory predicts that the logarithm of the current should vary as the square root of the applied field, which was not observed. Millikan and Lauritsen[2], however, found that a plot of the logarithm of the current against the reciprocal of the field gave a straight line. They then put forward a generalised form of Richardson's

equation in which emission depends partially on the field and partially on the temperature. This equation was discredited, however, as it was found that at low temperatures, the field emission is independent of temperature[3].

Time was now ripe for an explanation of field emission in terms of quantum mechanics, and this was given by Fowler and Nordheim[4]. The current density was calculated assuming first a triangular potential, and was subsequently made to include the electron image potential[5]. Field emission takes place by wave mechanical penetration of the potential barrier by the electron. The difference between field emission and thermionic emission is now apparent; thermionic emission requires the electron to have obtained thermal energy in excess of the work function of the surface, in order to escape over the potential barrier, whilst field emission is a demonstration of the wave mechanical size of the electron which allows finite probability of its location beyond the barrier (see figure 1B).

The Field Emission Microscope   Quantitative work on field emission in the 1930's proved very unreliable because of the difficulty of obtaining clean surfaces, free from protrusions. The most valuable work started with the introduction of the field emission microscope by Müller[6,7]. He obtained a sharp metal point by electrolytic etching, then heated the point electrically in vacuum to evaporate everything but the base metal. Tungsten was the metal normally used, for which the metal is far less volatile than its oxide or other surface contaminants. To clean a tungsten point it is normally heated to about $2500^{\circ}C$, in which process surface diffusion of the metal also takes place. The result is a clean,

round point, free from the impurities and irregularities that had troubled earlier work. The tip is then a single crystal, rounded to a hemisphere, so that if a fluorescent screen is allowed to surround the tip, an electron pattern can be observed which projects the emission from the various crystal planes around the tip. The work function of the 111 plane is less than for the 110 plane, and so forth, hence the electron current will be greater from the planes of lower work function, and there will be corresponding distribution of intensity on the fluorescent screen (see figure 2B). The pattern on the screen tells us the crystal category of the point and how it is oriented, in addition to a great deal of information about the surface condition of the point.

The Field Emission Tips The tips should have a radius of between 10^{-4} cm. and 10^{-5} cm. to give fields of the order of volts per angstrom with power supplies in the kilovolt range. Tips of radius smaller than $1000\overset{\circ}{A}$ are difficult to form directly, but tips can be sharpened by carefully regulated ion bombardment. Ions tend to strike the region towards the shank of the tip which has the effect of sharpening the point. However, excessive ion bombardment will destroy the tip. Points are normally produced by electrolytic etching, though satisfactory tungsten points can be made by simply burning the wire in a flame.

Observation of Single Atoms The field emission microscope enables one to observe single atoms. The resolution of the field electron microscope is of the order of $20\overset{\circ}{A}$ so individual lattice atoms cannot be observed, but the effect of a foreign atom on an otherwise clean

lattice surface can be readily observed. If ions are used instead of electrons, the resolution is increased by about a factor of ten, and is of the order of 3 to 5Å. With this resolution individual lattice atoms can be observed. The resolution is determined by two factors, the thermal velocity of the particle and its size. In both cases, the larger particles are favoured. The velocity of particles with a given thermal energy is proportional to the square root of their mass. A similar relation holds for the size of a particle; the wavelength is inversely proportional to the square root of the mass.

If a barium atom falls onto an electron emitting tungsten surface, it acts as a small protrusion and also reduces the work function in its vicinity, so that its presence is marked by an increase in electron emission from that point, and a bright spot on the screen. The field lines are almost radial, and if they do not bend, the electrons will follow them to the screen thus projecting the emission pattern of the metal surface. Other atoms such as oxygen effect a decrease in the work function of the surface. Even at pressures of the order of 10^{-8} mm. of Hg., oxygen will cover the tungsten surface in about a minute. Gas molecules become polarised in the field and are attracted to the tip because of the field's inhomogeneity. This means very low pressures must be attained if the point is to be kept clean for any period of time. The changes in work function from different atoms on a metal surface can be explained as arising from an induced dipole on the surface. Electropositive atoms such as barium repel electrons whilst electronegative atoms such as oxygen attract electrons, the average excess charge on the atom being less than one

electron. It is a general rule that atoms of low ionisation potential decrease the work function and atoms of high ionisation potential increase the work function. The rare gases act as dielectrics[8].

Field Ion Emission

Field emission of positive ions was first observed by Müller[9] in 1941 when he found that barium ions could be desorbed from a tip by reversing the electric field. At high enough fields tungsten itself will evaporate. This is so effective a method of cleaning the tip that it is often preferred to flashing. Evaporation of atoms from the substrate takes place at points where the field is greatest and where the atoms are most loosely bound. This means that atoms surrounding the major faces are first to evaporate, which results in far smaller areas of the main faces, particularly the 110 plane in points prepared by field evaporation than in those cleaned by flashing and formed by surface diffusion.

Field ion emission was first investigated in the hope that it would yield better resolution than was obtainable for electrons. The factors contributing to the resolution with electrons are the local disturbance of the field, and their wavelength. A point impurity will extend its disturbance of the field over an area greater than its immediate size. The wavelength of electrons is undefined at the surface, but falls to about $10\overset{o}{A}$ within $10\overset{o}{A}$ of the surface. To see if such an instrument was workable with ions, Müller performed the following experiment[10]. A tube was filled with hydrogen at 5×10^{-3} mm. of Hg. and the electron picture observed. The voltage was then reversed and increased several fold, under these conditions hydrogen ions go to the screen.

A supply of hydrogen atoms to the point was maintained by polarisation and attraction of the atoms in the inhomogeneous field. A resolution of about 5Å was obtained, which is almost sufficient to observe individual atoms in the metal lattice. The intensity of a field ion picture is very much less than that obtained with electrons, but a dark adapted eye can see it quite easily. Field ion microscope pictures are now taken with helium using tips that have been cooled to liquid helium temperature. The resolution depends on the random tangential velocity of the ions. The energy from the attraction of the polarised atom to the tip adds to the thermal energy, and will also contribute to the tangential velocity of the ions after collision with the tip. This effect is of major importance to the resolution, so that even helium, which is chosen for its low polarisability, acquires an energy of 0.1ev compared with 0.025ev of thermal energy. The tip is cooled in order that the gas may lose some of this energy on collision with the surface. Helium microscopes, although they give the best possible resolution, do not give such good intensity as would be obtained with other atoms. The low polarisability, means a smaller supply of atoms to the tip as the sphere of capture is smaller. Also, higher fields are required to maintain the current because of the high ionisation potential of helium. However, higher pressures may be used with helium than with other gases and this compensates to some extent for the other sources of poor intensity, though with some lack of definition from scattering by the gas.

Criterion for Ionisation Atoms are ionised in a region of from 5 to 20Å above the surface in a field ion source, and are not desorbed

from closer contact with the surface. The criterion that an atom may be ionised is that the energy level of the valence electron should not be less than the Fermi level of the electrons in the metal. Normally the ionisation potential is greater than the Fermi level which means that the atom cannot be ionised at a distance closer than $a = (I - W)/E$ where I and W are the ionisation potential of the atom and the work function of the metal respectively, and E is the field at the surface. This is further apparent from the fact that we need to supply an amount of energy $I - W$ in order to ionise the atom by transferring the electron to the metal, and this energy is provided by the field, i.e. $I - W = Ea$. At low fields therefore, ionisation takes place at distances further from the surface. However, if fields are sufficiently high, ionisation can take place in the region beyond the metal surface. This process is referred to as autoionisation. The potential well of the metal surface is then no longer instrumental in helping ionisation by its reduction of the barrier thickness through which the electron has to tunnel (see figure 1C).

A Pulsed Ion Source   It was thought that improved resolution would be obtained by pulsing the high voltage rather than applying a d.c. potential[11]. If microsecond pulses are applied at millisecond intervals, the atoms would not acquire the polarisation energy and would have had a chance to lose much of their thermal energy to the tip. The instrument now effectively becomes a field desorption microscope. However, the supply of atoms turns out to be very low in such a system, even when atoms which have a high sticking probability onto the metal surface are used.

<u>Energy Distribution of Ions</u> The energy distribution of field emitted ions has great importance in the adaption of such an ion source to a mass spectrometer. If the instrument is not double focussing, the homogeneity of the ion beam is a major factor in determining the resolution of the instrument. Inghram and Gomer[12] reported a 20 volt spread in ion energy from surface ionisation, which would give a resolution of 1 part in 150 for a mass spectrometer having a 3000 volt ion beam.

The energy distribution of the ions gives their location at ionisation. Atoms having nearly the full energy of the applied voltage will have been formed close to the metal surface, whilst those having less energy will have been formed further away from the tip. As the voltage is increased, a large proportion of ions are formed by auto-ionisation in the region beyond the surface, which increases the energy spread beyond 20 volts.

<u>A Mass Spectrometer Ion Source</u> The most serious attempt to adapt a field emission ion source to a mass spectrometer was by Inghram and Gomer[12]. They mounted a field emission tube of near conventional design opposite the exit slit of a mass spectrometer. A small hole, 0.75 mm. in diameter was made in the screen, through which a sample of the ions could be allowed to fall on the exit slit. The tungsten point itself served as the entrance slit, in that it was a point source of ions. The point was lined up with emission from about $900\overset{o}{A}^2$ of the 111 plane of the tip surface supplying ions. The pressure of gas under analysis in the field emission tube was 10 microns. The region between the hole and the screen was pumped in addition to the

analyser, which enabled a reduction of pressure by a factor of 100 at each stage, to a value of 10^{-7} mm. in the analyser tube.

Several common gases were introduced into the source and the yield of the molecular and other ions observed. Hydrogen gave 50% H^+ and 50% H_2^+, whilst oxygen and nitrogen always appeared in the diatomic state. Water gave almost equal amounts of $(H_2O)^+$ and $(H_2O)_2^+$, with traces of higher molecular groupings. Methyl alcohol gave mainly $(CH_3OH)^+$, but there was some $(CH_3O)^+$, the amount of which decreased as the field was increased. This indicated that the $(CH_3O)^+$ ion was formed at the metal surface and suggested some stronger binding of the molecule to the tip. Autoionisation appears to give ions of pure parent molecules without introducing fragmentation. Field ionised acetone yielded all parent ions. This may be contrasted with an electron impact source from which 19 different fragmentation products have been recognised. It is unfortunate that because of the need for good resolution we are not able to operate a source in the autoionisation region, but must employ surface ionisation and lower fields in order that the energy spread in the ions shall not be too great.

The instrument used was a 60°, 12 inch radius magnetic analyser, with electron multiplier detection. The electrical connections within the source were as follows. The stabilised accelerator potential was applied between the point and the grounded exit slit. A variable high voltage supply was connected between the screen and ground to provide the field necessary for ionisation. The excess energy was subtracted from the beam after it passed through the hole in the screen and approached the slit.

EXPERIMENTAL

Preparation of the Tips

Only tungsten points were used in this work, which were made by an electrolytic method. Other tips are more difficult to make. For example, platinum tips have to be electrolysed in molten salt. Tungsten is the most commonly used material for this work, though other workers have recommended rhenium because of its lack of affinity for oxygen, or carbon whiskers that are grown in carbon arcs.

The point is mounted on a tungsten hairpin in order to heat it in vacuum. The hairpin is constructed of 0.008 inch tungsten wire and a piece of 0.005 inch wire is spot welded to the loop to supply material for the tip. The 0.005 inch wire is threaded through a loop of platinum wire and is supported above by a metal clip so that the hairpin hangs vertically down (see figure 2C). The platinum loop is adjusted to be at a height of approximately 1 millimetre above the weld. A 6 volt potential is applied between the clips and the platinum, the clip being positive and the loop negative. Alternating currents can also be used. A drop of normal caustic soda is introduced into the region between the loop and the tungsten wire. As the small drop of electrolyte becomes exhausted, fresh alkali is added with a fine medicine dropper. A fine tip results when the 0.005 inch tungsten wire pulls apart in the region of electrolysis because of the weight of the hairpin. The weight of the hairpin is adjusted to overcome the surface tension of the droplet and to break the wire just before electrolysis is complete.

The hairpin is spot welded to a pair of electrodes by which the point can be heated in vacuum, a process known as flashing. When a tip is flashed, heating to high temperatures, say $2500^{\circ}C$ for short periods of a few seconds is preferred to heating to a lower temperature for a longer period, as the relative cleaning to surface migration is more favourable, so that there is less blunting of the tip. The shape of the point after flashing will be something between a hyperboloid and a sphere on a cone (see figure 2A). A good criterion for the sharpness of a point is that it is just unresolvable by an oil immersion microscope. Measurements of the tip dimensions for calibration of the field are made with an electron microscope. If the tip were perfectly spherical, the field at the surface would be V/R where V is the potential of the point and R its radius. The field becomes less towards the shank of the tip where the curvature is in one plane only.

The Ion Source

It was decided to use a conventional pattern in the design of the source. This meant constructing it out of glass. Plans for a metal source were drawn up, but abandoned because of the difficulty of lining up the point. Now that an auxiliary system for evacuating and lining up the point has been constructed, it may be worthwhile reconsidering designs for a metal source, which in the long run would be more satisfactory than the glass source at present being studied.

The source is constructed of pyrex and follows the design of conventional field emission tubes (see figure 7). The inside of the

tube has a conducting tin oxide coating[13] which makes contact with an electrode. Contact between the electrode and the conducting glass can be made by a small tungsten spring supported on the electrode and touching the glass. If an extra heavy coating of tin oxide is concentrated onto the region of the electrode, some contact between the metal and the glass will usually occur, which enables one to avoid the use of the rather inelegant spring. However, contact could sometimes not be made in this manner, probably because of the surface conditions of the glass-metal seal. Another procedure is to cover this area with aquadag or platinum paint. Aquadag requires that the tube be flushed with nitrogen or argon whilst the organic binder is being burnt off. For this reason, platinum paint is to be preferred. The tin oxide coating is produced by heating the glass in an oven to 400°C, then blowing stannous chloride vapour onto the surface. For the best results, the vapour should be mixed with steam from the salt and appear as thick white fumes. The coating thus obtained is very tenacious and cannot be removed by standard cleaning agents. It can be made to have an electrical resistance of the order of kilohms. The conducting surface is coated with phosphor. The phosphor is dispersed in a solution of nitrocellulose in amyl acetate and acetone, and the nitrocellulose later burnt off.

The stem of the tube is constructed of precision bore 7/8 inch pyrex tubing in order that it will locate accurately and firmly with the slit. In the upper portion of the stem there are two large holes in order to provide an exit for the gas other than through the analyser tube. Location of the source with the slit system is via a monel collar,

that has been machined to fit exactly inside the precision bore pyrex tubing. The collar is 1/2 inch high, of which only the lower 1/4 inch makes contact with the glass; the upper portion does not touch the glass. Too much overlap of the metal collar with the glass can not be allowed in order that the path from the electrode to the collar be as long as possible. The present arrangement gives a voltage gradient that was about one fifth that of dielectric breakdown in pyrex. The extra height given to the metal collar is to extend the ground potential region up as close as possible to the screen, so that the ions emerging from the hole in the screen enter into a region of ground potential as soon as possible. The length of the collar is such that the gas can escape through the side holes as shown in figure 7.

A jig was made to facilitate the geometrical alignment of the point during the final sealing of the glass ion source. When the upper and lower portions of the source are sealed together, the point, the hole in the screen, and a 3 mm. hole in the centre of the jig can be lined up by eye, by observing that they appear concentric.

Some thought was given to the possible advantages of employing a slit system with focussing properties. It was, however, decided this would be an unnecessary complication at this stage. The field emission tip is a point source, which, together with the entrance slit to the analyser defines the ion beam quite effectively. Consideration was also given to the idea of a strong focussing source system, using quadrupole electric or magnetic fields (see figure 3). One of the attractions of such a system is that it will focus a beam of circular cross section into a ribbon. Successive crossed quadrupoles give

positive focussing of the beam, a principle that is used in high energy machines. Magnetic fields are more effective at bending high energy beams than are electric fields, and are therefore used more often than electric fields in this connection; however, Giese[14] has constructed an electric quadrupole system for an ion source.

Vacuum Technique[15]

A way must be provided to determine whether the tip is sufficiently sharp to give the required field and whether it is oriented to give a good supply of ions in the direction of the slit. The method is to observe the electron pattern from the tip, since the ions will come off from the same regions as do the electrons. However, to observe an electron pattern, a very good vacuum, preferably of the order of 10^{-8} mm. of Hg. is required. At this pressure, clean tungsten becomes covered with oxide in a time of the order of a minute, and at higher pressures bombardment of the tip by positive ions may spoil the point and initiate a vacuum arc. The first problem was therefore to obtain a high vacuum.

High vacuum technique has advanced considerably over the last ten years, less from a development of new techniques than from a general realisation of the factors that limited the vacuum under the old techniques. The necessity of having a system that can be baked out has become well recognized; this has been accompanied by the replacement of rubber gasket materials by soft metal, and of greased glass stopcocks by metal valves. Cold traps have been made more efficient by packing them with copper foil[16] to prevent back streaming of oil diffusion pump vapour which would otherwise limit the pressure to

10^{-7} mm. of Hg. There have also been improvements in ionisation gauge design[17] which enables pressures below 10^{-10} mm. of Hg. to be measured. The new design has a thin wire anode which obviates the limitation on the previous design where the anode photoelectric current, from photons formed by the thermionic current to the grid, would swamp the ion current.

Ion Pumping[18] It has long been realised that an ionisation gauge acts as a pump. Workers in field emission keep their ionisation gauge running continuously in their sealed off gettered systems. The remaining gas in the tube is ionised and driven into the walls of the tube. Helium has the ability of diffusing through pyrex which would limit the pressure if ion pumping were not used. A water cooled ion pump was constructed on this principle but was not used, as a commercial ion pump became available. The ion pump consists of a central tungsten wire cathode surrounded by a widely spaced spiral molybdenum wire grid (see figure 4A). A thermionic current flows between the heated cathode and the grid, from which ions are formed by electron bombardment. By virtue of the cylindrical geometry, the electrons receive most of their energy close to the wire and travel at nearly their full energy over a wide cross section of the tube. The glass walls serve as an anode; its potential is the same as the cathode, otherwise an electron current will flow. Also, by reason of geometry, a field gradient such as to cause the majority of the ions to travel to the walls rather than go to the cathode prevails across most of the tube. The grid could be degassed by resistance heating.

The VacIon Pump[19] A Varian VacIon pump was purchased for evacuating the auxiliary chamber. The pump operates on a Penning cold cathode

discharge as is used in the Phillips Ionisation Gauges. The design makes use of a magnetic field which controls the direction of motion of the electrons, and causes them to cover a far longer path in getting from the cathode to the anode than would be the case if there were no magnetic field (see figure 4B). Hence the density of the discharge is far greater than it would be without the magnetic field. The currents are therefore higher and more effective in cleaning the vacuum system. The cathode is made of titanium which is sputtered by the ion current. These freshly sputtered titanium atoms are very effective as a getter, and play an important role in trapping the gas atoms. The current is supplied by a 3KV power supply and is measured by a logarithmic meter. Since the current is proportional to the pressure, the scale is also calibrated in millimetres of mercury so that no auxiliary pressure gauge is required. At 10^{-8} mm. of Hg. the pump current is 1 micro-ampere, which is the limit of current that can be measured by the meter, so that this is effectively the lowest pressure attainable. The pump current falls off as the pressure decreases, as is to be expected since the residual gas maintains the discharge.

Because of the active titanium gettering surface, it is ad-visable to keep the pump sealed under vacuum when not in use. The pump is in fact received in this condition from the makers. This necessitates the installation of a valve to seal off the pump when it is not in use. If it is necessary to allow the inside of the pump to come to atmospheric pressure, it is preferable to let it up with dry nitrogen than with moist room air. When re-evacuating a system that has been let up to atmospheric pressure, the pump evolves a lot

of gas that has been trapped on the gettering titanium surface, and from the colour of the discharge, the most firmly absorbed gas is not nitrogen, but probably water vapour.

Restarting the pump after it has been let up to atmospheric pressure requires a fairly slow procedure. It is not possible simply to pump the pressure to below 10^{-4} mm. with the backing pump, seal off the system, and switch on the ion pump, because as soon as the latter starts to function, a great deal of loosely adsorbed gas is evolved into the system which would be difficult to remove by the ion pump. The best procedure for starting is to bake out the pump under reduced pressure at between 300°C and 400°C. However, this is not normally possible because of the presence of the magnet. By mounting two 250 watt infra red lamps at a distance of 3 inches from each side of the pump, it was possible to obtain a baking out temperature of 360°C.

When bake out is not convenient, the following procedure is used for restarting the ion pump after it has been exposed to atmospheric pressure. The system is first pumped to a pressure of about 10^{-4} mm. of Hg. by means of a mechanical pump provided with a liquid air trap. The ion pump is then switched on for periods of about 5 seconds, time being allowed between each period for the gases evolved to be removed by the mechanical pump. As the ion pump becomes degassed it may be left on for longer periods. The ion pump gradually becomes degassed sufficiently to be left on continuously. When degassing is complete, the system is sealed off. It normally takes up to half an hour to start the pump.

The Auxiliary System

An auxiliary vacuum system was constructed for the purpose of testing and lining up the ion source point. In this system a glass evacuation chamber was used in order that the electron pattern of the tip could be observed. As a high vacuum, 10^{-8} mm. of Hg. was desired, metal gaskets were employed throughout so that the apparatus could be baked.

The chamber in which the source is tested, is constructed of a 3 inch kovar-pyrex seal, argon arc welded to a stainless steel flange (see figure 5A). The source can be viewed through a pyrex plate in the top of the chamber. The lower flange holds the electrical and pumping leads. The chamber is fitted with three 1/4 inch kovar-pyrex seals for electrical leads and one 5/8 inch central pumping lead. Two additional electrical leads are provided by a two wire glass press seal. The leads in this form also provide a convenient way of mounting the source inside the chamber; the leads are joined to the source leads by small nickel tubes which gives mechanical support as well as making the electrical connection.

The Vacuum Gasket Lange and Alpert[20] have reported a high vacuum gasket joint using a step type of seal which was used successfully at pressures of 10^{-10} mm. of Hg. with successive heat cycling to 400°C. A slight modification was made to this design as a means of limiting the depth of cut by the step. Lange and Alpert have the two flanges touch when cutting is to a sufficient depth, whereas in the present arrangement, the gasket is made slightly thicker than the depth of the step so that cutting is limited by the pressure being taken up by the wide area

of the gasket (see figure 5B). The flanges are secured by 6 bolts
and the gaskets are cut from 0.040 inch aluminium. Pure aluminium is
not available in the form of annealed sheet, so 2S0 grade is used.
The gaskets are cut from the sheet by a specially made die, using a
screw press to force the cutting. A pure grade of copper is normally
used for gaskets, but aluminium is more easily obtainable and equally
satisfactory at the temperatures used for bake out, which are normally
below 400°C.

Layout of the Auxiliary System   The chamber was mounted on a board of
half inch transite and baked out by means of a nichrome wire furnace.
The remainder of the system was flamed out with a bunsen burner. Since
very low pressures are required, grease stopcocks and mercury valves
were avoided. There was the choice of using metal high vacuum valves[21,22]
of which many good ones have been designed in the last 10 years, or to
use glass seal-off systems. Most high vacuum valves have only a small
aperture through which pumping can take place, which, although it should
not affect the ultimate pressure achievable in a leak tight system, it
will affect the rate at which it is reached. These valves work on the
principle of forcing a cone into a bearing of soft copper or silver,
with sufficient pressure to distort the soft metal surface to allow
no leakage. It naturally requires less effort to seal off a small aper-
ture by this means, than it does for a large one. For this reason, most
valves do not have an aperture of more than 3/8 inch. The valve used
for sealing off the system from the backing pump was a Hoke, number 413,
whose aperture was 1/8 inch diameter. Metal vacuum valves are either
bellows or diaphram sealed, so that no gas can leak in from the atmosphere.

However, the backing pump is always kept running when the system is sealed off in case the closing action of the valve is not perfect. A valve of larger aperture is desired to join the ion pump to the chamber in order to secure a good pumping rate, so since a reasonably priced large aperture valve is not obtainable, it was decided to use a glass breakseal system (see figure 6). A battery of 8 breakseal tubes are mounted between two manifolds. These are drawn out so that breaking and resealing of their thin ends could provide a convenient way of letting the system up to atmospheric pressure. There is a side pocket on the tubes in which the iron breakers are stored.

The source is mounted on the filament leads inside the chamber. The glass source is retained in two parts until testing showed the tip to be satisfactory. A sheet of conducting glass was placed over the top of the ion source so that ions emitted from the tip and passing through the hole in the screen could be detected. The electron pattern could also be observed through the glass plate. The conducting glass was later replaced by a small Faraday cup of aluminium foil to reduce electrical leakage.

Testing Procedure   After degassing and baking out, the system could be evacuated to 10^{-8} mm. with the ion pump. The point was then flashed and the high voltage applied so as to give an electron pattern on the screen, which shows the quality of the tip and how it is oriented. We require a liberally emitting region of the tip to give emission in the direction of the hole in the screen; gas ionisation proceeds from the same areas as the electron emission.

Ion Current Measurement   The ion current from the point was measured

by a vibrating reed electrometer. The current was sufficiently large that the rate of charge method was not applicable, so a 750 megohm resistor was placed across the electrometer terminals, and the voltage developed across it measured. The order of magnitude of the currents measured was 10^{-8} to 10^{-9} amperes. The beam current in a mass spectrometer would be approximately one hundredth of this if a 0.25 mm. exit slit were used. The results of ion current measurement in air at 10^{-3} mm. of Hg. are shown in figure 8.

USES OF THE FIELD ION SOURCE

The field emission ion source can be used to give pure parent ions of organic and other molecules, for mass spectrometric analysis. Ionisation by electron tunnelling supplies just the needed amount of energy without further disturbance or excitation of the molecule, hence we find our ions free from disintegration fragments. In certain circumstances, fragmentation may require less energy than ionisation, but fragmentation will still not occur because the two component radicals in the molecule are too close together for the dissociation energy to be provided by the product of the field and their distance apart. A molecule in this category will almost certainly fragment when it becomes deionised. We observe CH_3O^+ ions from methanol; it is not likely that the hydrogen of the chemisorbed methanol is more tightly bound to the metal surface than it is to the oxygen, but it is probable that the chemisorption binds the hydrogen within the minimum distance of ionisation, so that ionisation takes place through the more distant oxygen. It is to be noted that fragmentation, where the electron relocates itself within the molecule, is not aided by the work function of the metal, as is ionisation where the electron moves into the metal.

The species of ion given by certain gases or gas mixtures might give some insight into the catalytic processes on metal surfaces. A platinum point would likely be of the greatest interest, and the field could be pulsed with short infrequent pulses, in order that the experiments do not suffer from the unknown perturbing effect

of the electric field. One could also study the adsorption reaction
on different crystal planes, and measure sticking coefficients for
different substances on different planes. All materials may be de-
sorbed from a field emission tip, and by applying a high enough field
the metal substrate will itself come off. Gomer reports that high
negative potentials on the tip will desorb material as negative ions.

The simplicity of field ion spectra makes the source ideal
for analysis of gas mixtures by mass spectrometry. If reacting gases
are introduced into the source, short lived intermediates may be
detected by virtue of the purity of the normal ion spectrum. The half
lives of excited states could be measured by having a potential on the
point, large enough only to ionise excited states, which have a lower
ionisation potential. Excitation could be by shining light onto the
tip.

Field emission offers a means of producing ions without
destroying the original state of the molecules. Thus a true
picture of the state of affairs around the point source is given.

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POTENTIAL ENERGY DIAGRAMS   Fig. 1

ELECTRON EMISSION
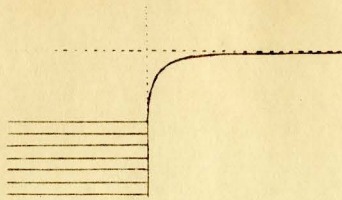
Image potential
at metal surface
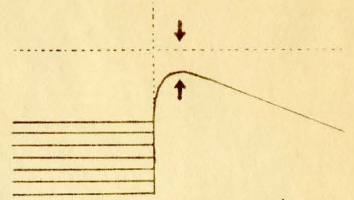
Schottky barrier
reduction by the field
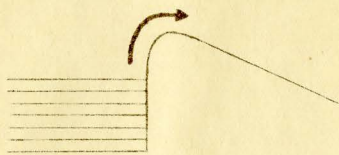
Thermionic emission
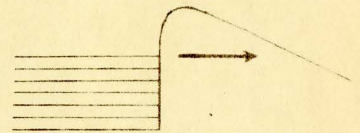
Field emission

ION EMISSION
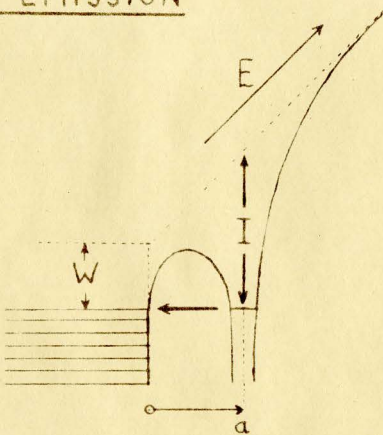
Ionisation
at metal surface
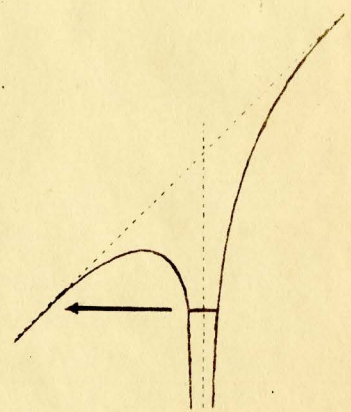
Autoionisation

E = field

W = work function

I = ionisation potential

a = separation distance

SHAPE OF TIPS

A
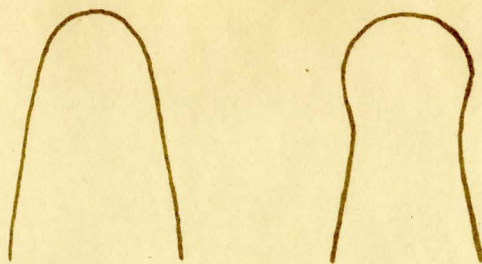
Hyperboloid   Sphere on a cone

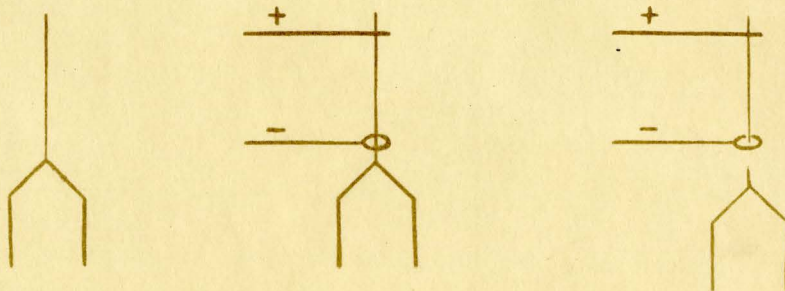## EMISSION FROM DIFFERENT CRYSTAL PLANES

B
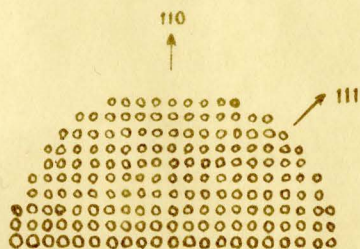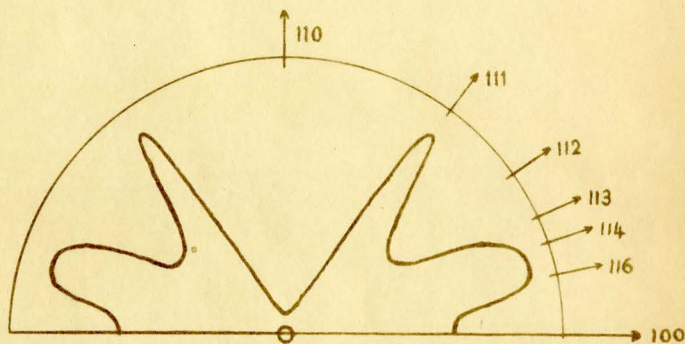
The atomic picture   Polar diagram of relative emission

ELECTROLYTIC ETCHING OF THE POINT

C

QUADRUPOLE FOCUSSING Fig. 3
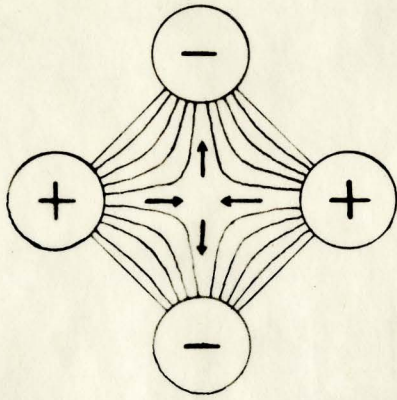
Electric quadrupole
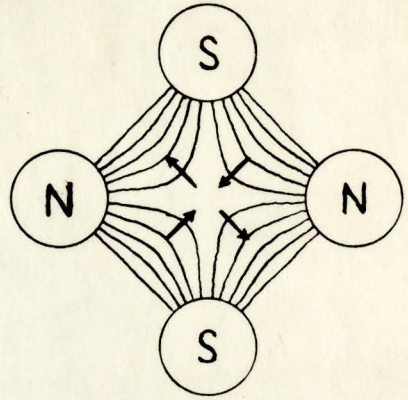
Magnetic quadrupole
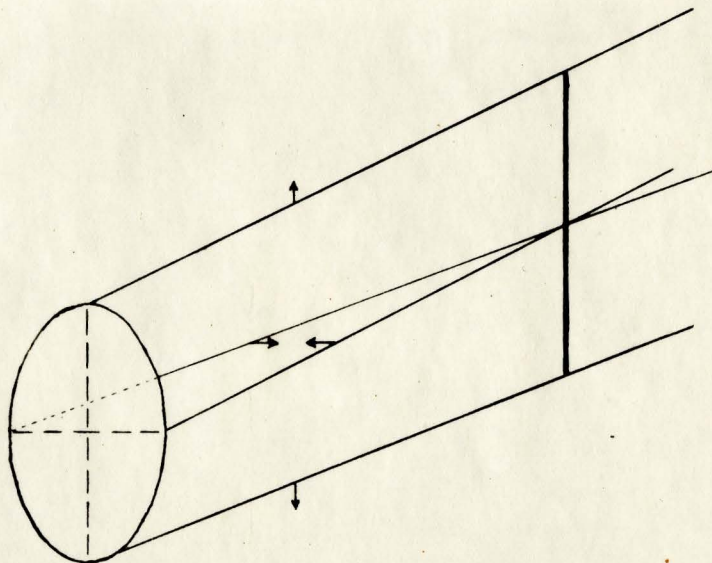
Focussing a beam of circular

cross section into a ribbon

THE ION PUMPS   Fig.4

THE IONISATION

GAUGE TYPE

A
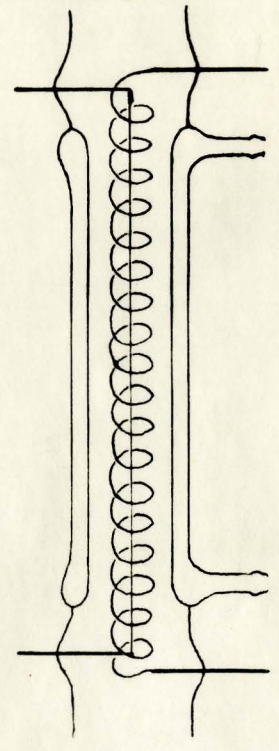
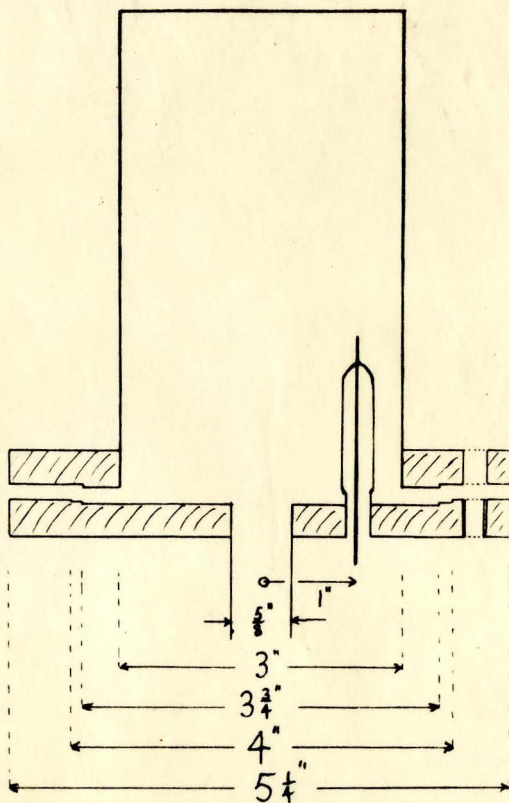0.008 inch tungsten filament

0.015 inch molybdenum grid

THE VACION PUMP

B

N

————————————— CATHODE

| | | | | | ANODE
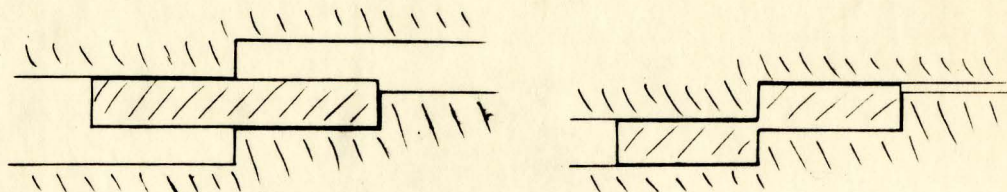
————————————— CATHODE

S
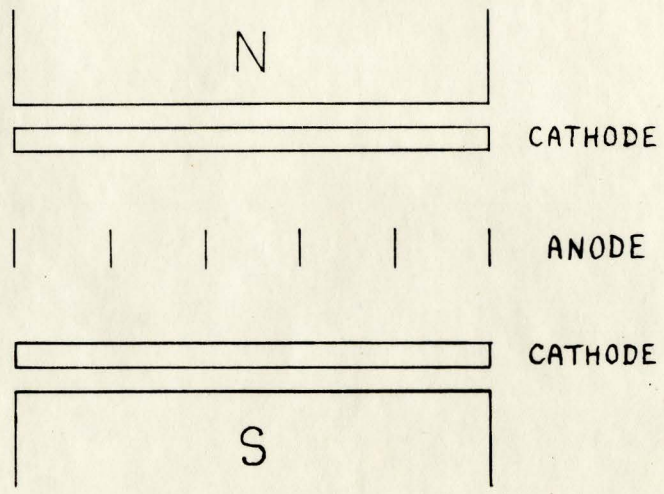
THE AUXILIARY CHAMBER Fig. 5

A

HALF FULL SCALE

5"

5"

3"

3¾"

4"

5¼"

¾"

1"
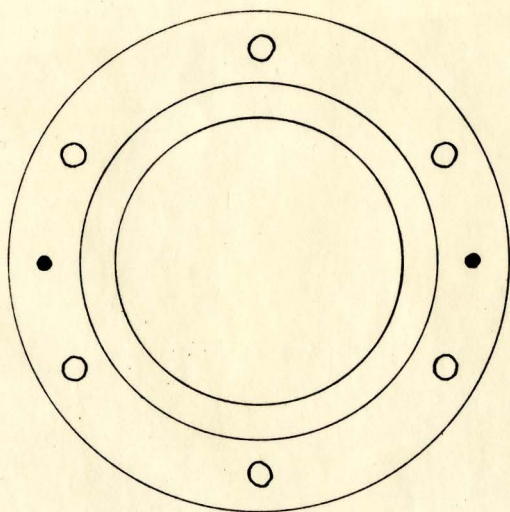
TOP FLANGE
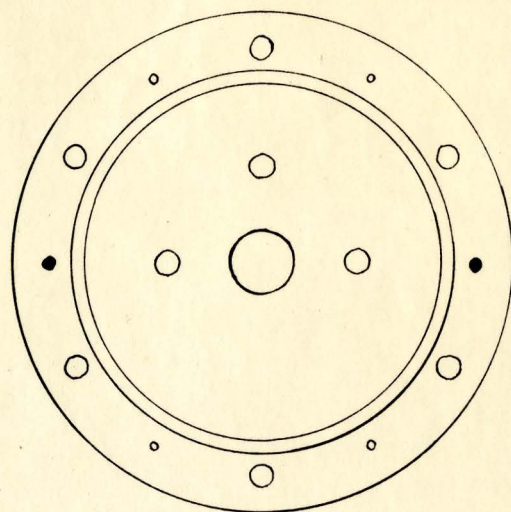
BOTTOM FLANGE

THE VACUUM GASKET

B

THE AUXILIARY SYSTEM   Fig. 6

AUXILIARY

CHAMBER

METAL
VACUUM
VALVE

BREAKSEAL

SYSTEM

ION
PUMP

LIQUID AIR
TRAP

TO
BACKING
PUMP

THE ION SOURCE   Fig. 7

TWICE
FULL SIZE

final
seal

monel collar
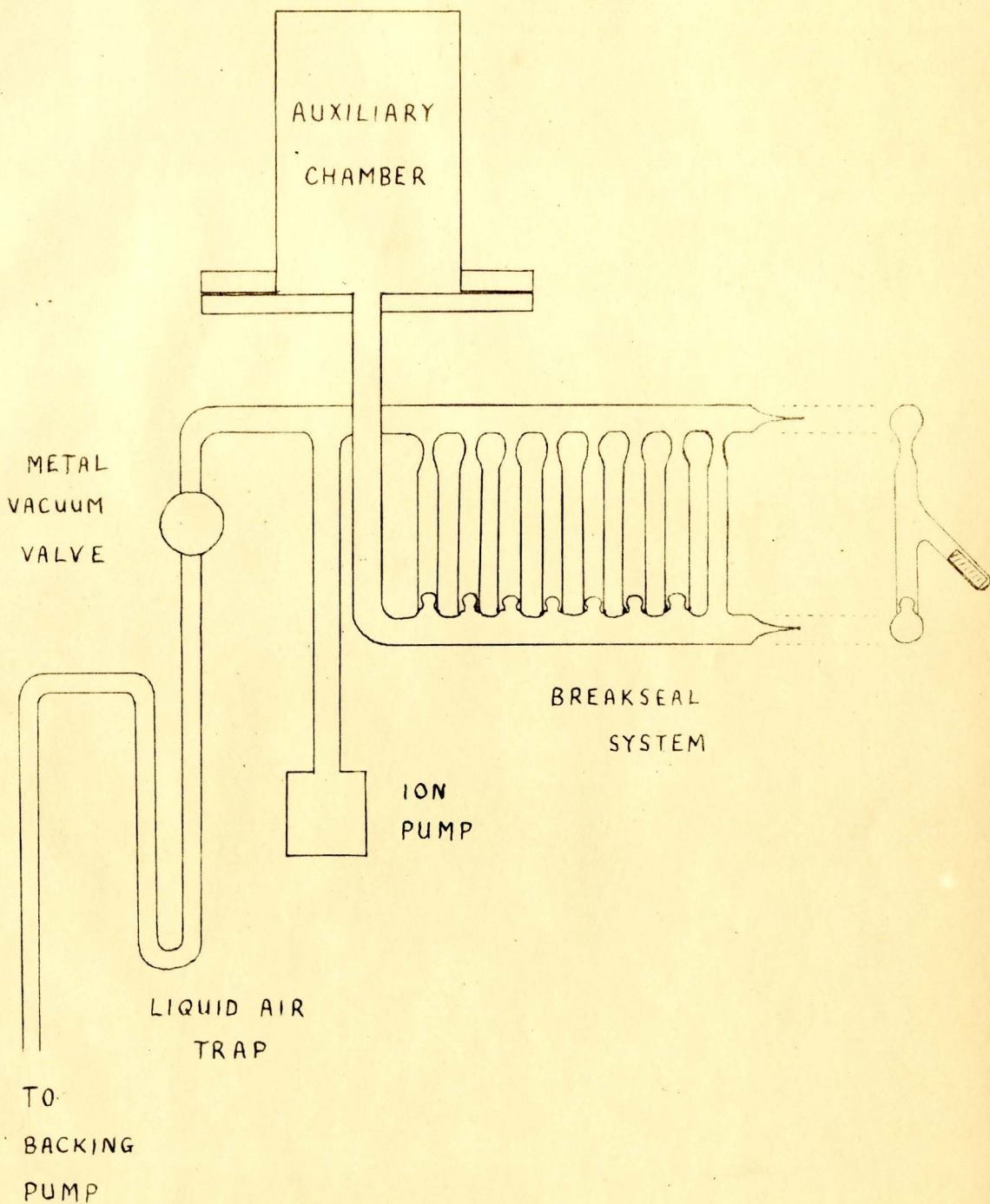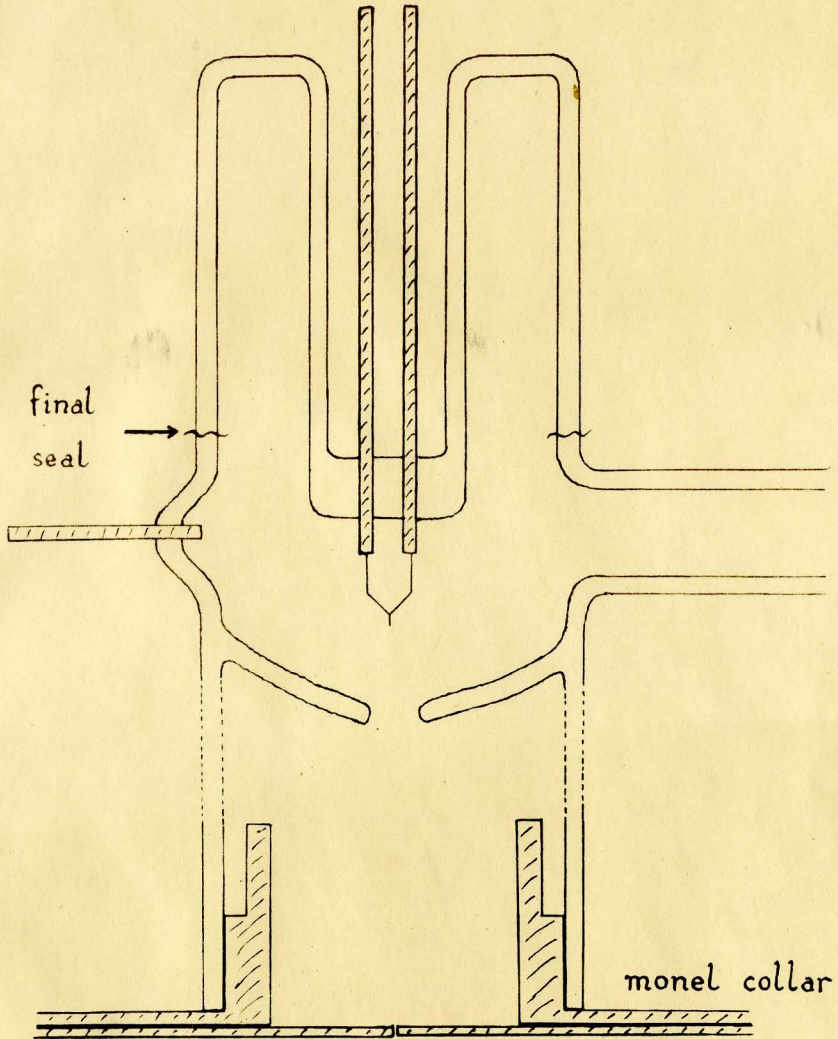
ION CURRENT MEASUREMENT Fig. 8

Air at 10^{-3} mm. of Hg.

ION CURRENT , AMPS.

TIP VOLTAGE KV.