A Modified Aston type Mass Spectrometer for the Investigation of Ionization Resulting from Single Impact

Thesis by
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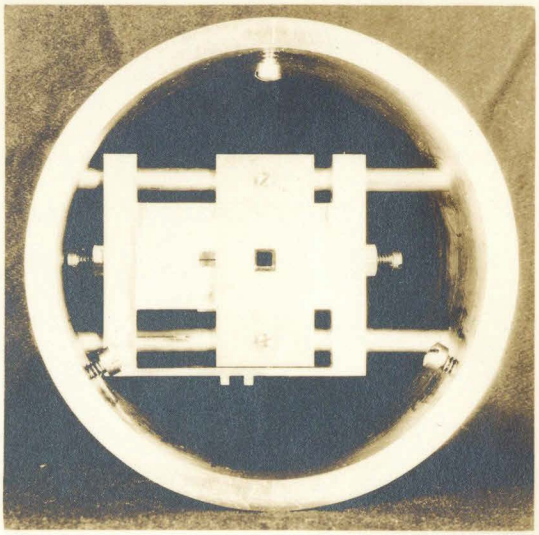
SUMMARY

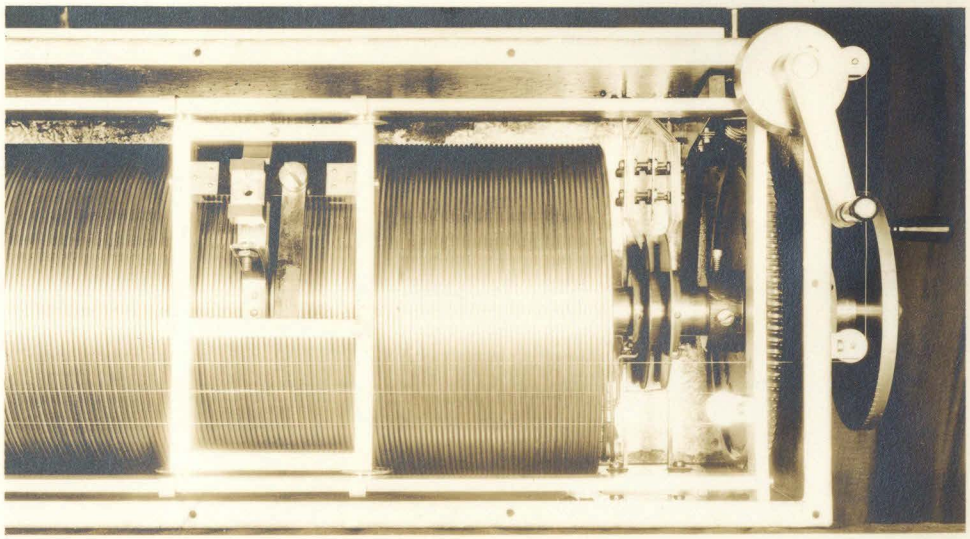
A modification of the Aston type mass-spectrometer is described for the examination of the process of ionization. The chief modifications provide for ionization by electron bombardment and for electrometric registration of ions. The various peaks are focussed individually on the collector by variation of the magnetic field. Details of the apparatus are given.

The focussing proved to be very poor, and the reasons for it are discussed. Also a partial correction of the focus was accomplished and results are given taken both before and after this correction. Specimen curves are given of the ionization in nitrogen, carbon monoxide, ammonia, and a mixture of three parts hydrogen to one of nitrogen.

A pliotron circuit is described with which a sensitivity of 2×10^{-17} amperes per scale division is regularly attained.

A new apparatus has been designed to eliminate the difficulties found in the first one, and certain additional features are included which should permit a more complete interpretation of the results. The analysis of the design of the magnetic field is given. A new type of balance is described which gives a continuous indication of the square of the magnetic field. An apparatus has recently been built according to the new design but is not yet in operation.





An extraordinarily powerful means of investigation was opened to physics when F. W. Aston announced his modification of J. J. Thomson's parabola method of positive ray analysis. Positive ray technique permits the investigation of individual particles (atomic or molecular ions) instead of revealing only the average properties of a large number of such particles, and the apparatus and technique devised by Aston advanced such investigation to a high degree of accuracy, permitting precise comparison of the masses of different isotopes. The positive ray method also lends itself admirably to the identification of ions produced in various ways and even offers hope of yielding quantitative chemical analyses where ions of the unknown substance can be conveniently produced.

It was found very early that positive rays could be deflected by either electric or magnetic fields and an observation on either deflection will yield a value of e/m provided the energy of the particle is known. However sufficiently precise knowledge of this energy is hard to obtain so that a method is very desirable which will be independent of the energy. By means of an electric deflecting field it is possible to select a beam of positive rays all of which will have the same energy to any reasonable degree of approximation, and by means of magnetic deflection it is possible to similarly select for uniformity of momentum, and by means of a series of high frequency electric fields as devis-

ed by W. R. Smythe it is possible to select for uniformity of velocity but these methods all involve a very great loss in available intensity and consequently are justified only in work of the highest precision. The method developed by Aston consists in combining both electric and magnetic fields so as to annul (within a comparatively narrow range of velocities) the effect of velocity. Essentially this is accomplished by using an electric field to spread the collimated beam into an energy spectrum and then picking out a narrow region of this spectrum with a stationary slit of adjustable aperture. Inasmuch as Aston uses an induction coil both to produce and accelerate the ions, there will be ions present corresponding to any desired energy selection within a wide range and since photographically all the different kinds of ions are recorded simultaneously, the energy to be selected can be chosen almost arbitrarily. However if electrometric recording is to be the choice only one kind of ion can be recorded at one time and the energy region selected should be free of fluctuations which might selectively affect certain kinds of ions, or comparative readings will be very difficult to obtain. It is worthy of mention also that the use of an induction coil introduces an implicit relation between the energy producing ionization and the energy possessed by the ion in its passage through the mass-spectrometer.

The Aston type of mass-spectrometer was chosen for this research because it avoids the assumption which is inherent in some other types that all ions enter the

analyser after having fallen through precisely the same potential difference. This assumption can be closely approximated under some conditions but it was undesirable to be restricted to these conditions. Greater precision is attainable by the use of a velocity filter as in Smythe's mass-spectrometer but convenience is to be preferred to such precision in the present work.

Certain features of Aston's apparatus were not entirely suited to the study of ionization and were modified as will be discussed below.

It was particularly desired to investigate ions produced by electron bombardment so a hot filament was introduced as a source of electrons. Originally the filament was supported on tungsten hooks imbedded in a pyrex mounting but radiation from the filament heated the pyrex to the decomposition point so fused quartz of a different design was substituted. The new design shielded the filament much less completely so that when thoriated tungsten was used it was soon deactivated by bombardment with negative ions. A still better style of filament mounting was made from lavite which rigidly and conveniently supports filament, grid, and filament shield. It is very convenient to join the lavite to the pyrex through a ground joint but the thermal expansion of lavite is greater than of pyrex so the lavite should surround the pyrex if the joint is to undergo any appreciable temperature change. The improvement now needed most in the filament is to eliminate the potential drop through the filament so that the bombarding electrons will be of more nearly uniform energy and

this will be attempted in the new design. The filament used is circular and surrounds a concentric cylindrical grid of wire gauze so that the electrons are accelerated radially inward in the plane of the filament. The filament shield is of thin sheet metal and contains a hole slightly larger than the grid. It is supported parallel to the filament and slightly further from the filament than the distance between filament and grid. The shield may be operated at the potential of the grid but it is convenient to be able to vary it if desired.

The filament current is supplied by a storage battery; the accelerating voltage for the electrons is obtained from a small motor generator set and both these supplies must be insulated from ground for the potential applied to accelerate the positive ions since it is necessary to have the body of the apparatus at zero potential.

The accelerating potential for the positive ions is obtained from a small dynamotor using a storage battery for the primary input. This potential is applied between the filament shield and the front slit of the collimator. Experience has shown that even without using a filter to cut down commutator ripple etc. the energies imparted to the ions by the potential all lie within a fairly narrow region provided the conditions in the discharge prevent any visible glow. Therefore by suitable choice of the deflecting potential almost the entire collimated beam will traverse the analyser thus yielding very good intensity. The condition of no visible discharge places limits on the electron cur-

rent, the bombarding voltage, and the gas pressure, and these quantities are so interrelated that variation of one will change the permissible values of the others.

Due to the comparatively low maximum energy of the ions it is possible to use larger deflections than were feasible in Aston's work so an electric deflection of one quarter radian and a magnetic deflection of one radian were chosen. The ratio of four to one between the deflections was preserved because of the rather remote possibility of using photographic recording at some time, in which case this ratio gives linear mass dispersion.

Careful attention was also given to the theory of the mass-spectrometer as worked out jointly by Aston and R. H. Fowler in an attempt to utilize second order focussing and this resulted in making the trailing edge of the magnet concave with a radius of 84mm but as will be shown later the focussing was very seriously in error.

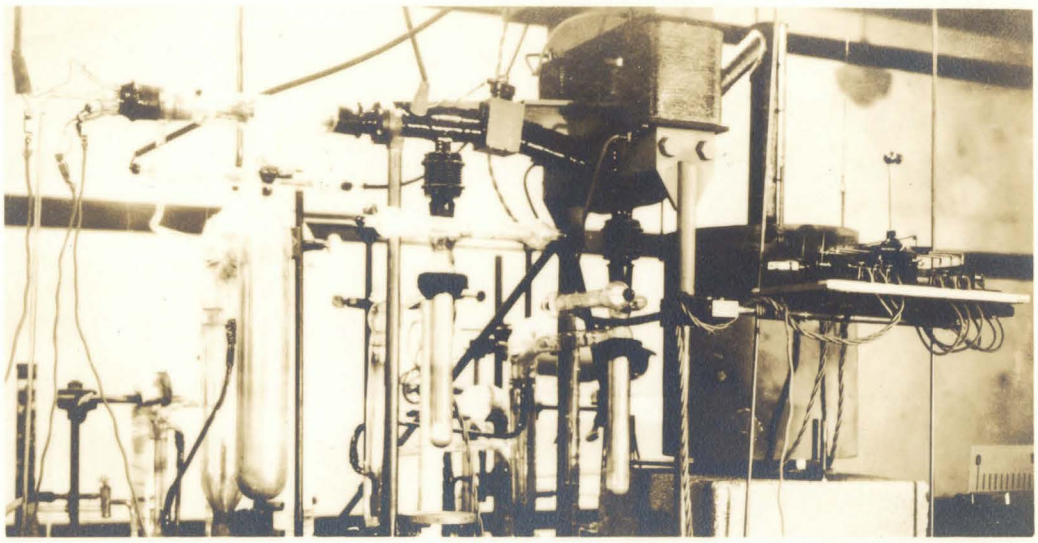
The upper panel of plate II shows a photograph of the old apparatus as set up with the necessary auxiliary equipment. The details of the mass-spectrometer are rather obscured by the mass of the magnetic circuit but the collimator is contained in the horizontal tube extending to the left from the electric field. Also shown is the triple walled cylindrical iron shield for protecting the electrometer from the stray field of the magnet. Just in front of the shield is the magnetically controlled switch for the various electrometer

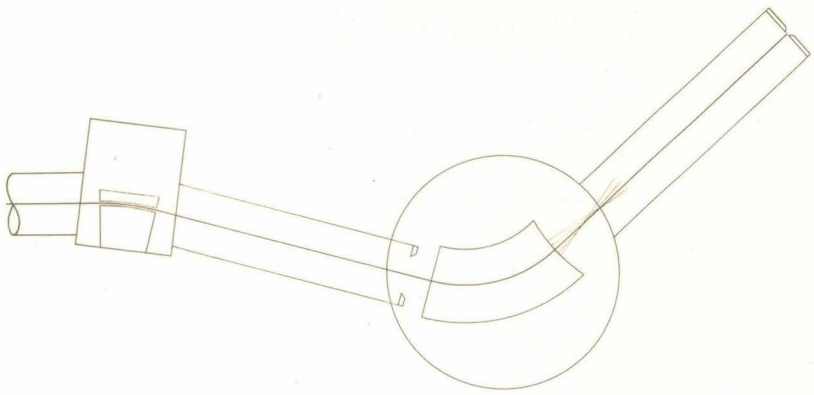
potentials. Because the mass-spectrometer is divided into three compartments by the collimator slits it is necessary to use a multiple pumping system. Since gas is being constantly admitted to the ionization chamber greater pumping capacity is required there and an extra large second stage pump is combined with a regular size first stage. Two regular second stage pumps served by a single first stage pump are used as scavengers, one connected to the collimator and one to the magnet box.

The gas to be studied is contained in a two liter reservoir and admitted to the apparatus through the capillary tube seen rising vertically at the extreme left of the picture. This tube is continued within the ionization chamber and its end lies on the axis of the grid in the plane of the filament so that the concentration of gas molecules is highest at the point of impact with the electrons.

The design data for this apparatus indicated that it should be capable of very good resolution so it was a great disappointment to find that even under the most favorable circumstances the peaks were so broad as to extend over several units of molecular weight. Also provision had been made for an adjustment of the focal slit along the median ray so that it could be located at the point of sharpest focus and even this adjustment failed to have any effect. Careful consideration of the paths of the ions seemed to indicate that the difficulty lay in the magnetic field so it was investiga-

ted more carefully. The uniformity of the field between the poles was seen to be rather poor due presumably to the fact that the pole faces were not solid but were made of two pieces soldered together because stock of sufficient size was not available. However this was not at all sufficient to account for the observed error in focus so a graphical investigation of the form of the pole faces was undertaken. On the assumption of perfect collimation a rough approximation could be obtained for the energy of a particle in terms of the deflection it suffered in the electric field and this value of the energy permitted the calculation of the radius of curvature of the path in the magnetic field. Neglecting edge effects in the magnetic field this circle of curvature would be tangent to the straight path at the leading edge of the field and a system of tangents at the trailing edge should show the subsequent behavior of the rays. The lower panel of plate II indicates the result. The electric and magnetic fields and the focal slit are shown, also the emergent tangents of four rays obtained as above, and the focal error is indeed surprising. There is no point focus at all, and the best focus of the caustic is almost 1.4 cm from the intended focus. A temporary mounting for the focal slit and collector was made to fit the new location and the focus was found to be much improved but still poor on account of the caustic. The new location of the collector also added considerable capacity to the tube circuit and made readings very slow. Previous to the graphical investigation slits had been tried at





the edges of the magnetic field and produced little benefit when used at the trailing edge. At the leading edge they would produce sharper peaks but only at the sacrifice of much intensity, as would be expected from the great divergence of the rays at the intended focus.

The theory of the mass-spectrometer shows that the molecular weight of an ion is proportional to the second power of the magnetic field which brings it to the focal slit, so the identification of the ions depends on a knowledge of the magnetic field. Since it would be very convenient to have a continuous indication of the field it was originally hoped that measurement of the current in the magnet would give some rough idea of the strength of the field, provided each cycle started from some standard magnetic state. However it was soon found that even if there had been exact proportionality between current and field strength, much greater precision in the measurement was required than could be attained with an ordinary ammeter, and furthermore hysteresis was not negligible. Next an external air gap was improvised and a calibrated bismuth spiral was employed whose resistance was measured with a Carey-Foster bridge. This gave usable results but laborious corrections were required for temperature. The effect measured is a change in resistance due to the magnetic field but this effect has a temperature coefficient and there is also the usual change in resistance due to the

temperature alone so the necessary corrections were of quadratic form. An essential datum is the resistance of the spiral in zero field at the temperature of the subsequent readings. Since in the air gap the spiral was closely surrounded by massive iron, its temperature there might be quite different from that found in the air outside the gap, and it was impracticable to reduce the field to zero at frequent intervals to determine this quantity. Thus it was found necessary to build a very flat platinum resistance thermometer which could be permanently installed in the air gap beside the bismuth spiral and its resistance was conveniently measured on the same bridge. All this greatly complicated the observations and the calculations so it was finally given up when it was found that the calibration of the spiral was not entirely reliable.

The next step was the use of a snap coil connected to a ballistic galvanometer. This was calibrated by indirect comparison with the large Zeeman effect solenoid and gave rather consistent results but was unsatisfactory because it required to be manually cocked and tripped for each reading, and also jarred the pliotrons sufficiently to interfere with their operation.

A brief attempt was next made with a wattmeter in the magnet circuit for it would give indications proportional to the square of the current and so approximately to the square of the field but again sufficient precision in reading could not be attained. The lower panel of plate III, in the curve running upward to the right, shows how the precision falls off at low fields.

All four curves are plotted against a linear scale of rheostat settings, and the break in each is due to the change in the material of the winding. In the group of three curves, the lowest represents watts; the highest, ballistic galvanometer deflections; and the intermediate curve represents the square of the ballistic galvanometer deflections. The fourth curve is the reciprocal square root of the watts, and so is necessarily proportional to resistance, consequently it should continue straight to the end if the readings were accurate enough.

The satisfactory and final solution of the problem is discussed in connection with the new apparatus.

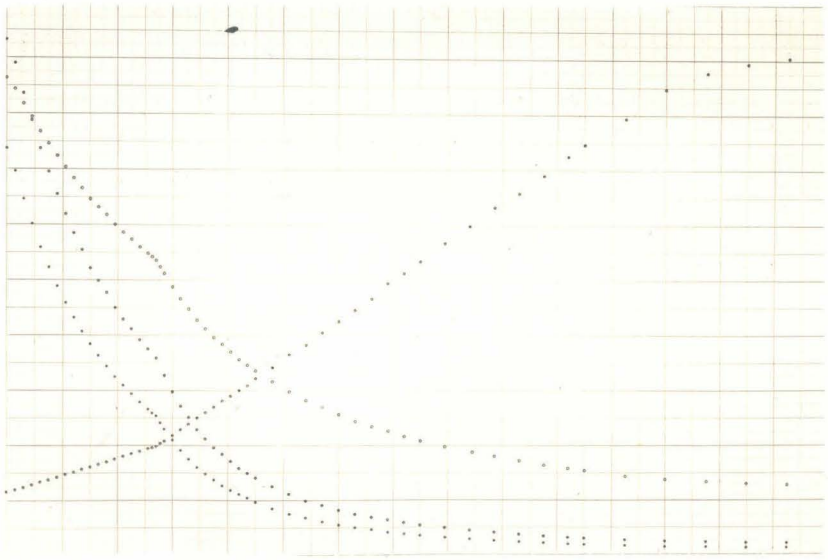
Because of the difficulty of quantitative interpretation of photographic records of mass spectra (except in the case of isotopes of the same element) electrometric registration was planned from the start. The first attempt was made with the Hoffmann vacuum binant electrometer and much time was expended on getting it to operate. Only amber or quartz insulation could be permitted on the lead from the collector to the electrometer and the lead had to be run in vacuum all the way to prevent its picking up atmospheric ions. Much trouble was experienced with the tilting switch due to its inferior design, and a stable mounting for the instrument was arranged only by suspending a heavy concrete block from the ceiling. Also to prevent transmission of vibration from the mass-spectrometer to the electrometer the vacuum shield around the lead had to

be divided into two parts and the connection between the parts run exposed to the air although it was closely shielded so that it could pick up ions from only a very small volume. All this was accomplished satisfactorily but the really serious difficulty came from the stray field of the magnet. The mechanical control in the Hoffmann is quite small and is partially cancelled by an electrical control, consequently, since the needle is made of a diamagnetic platinum-iridium alloy, it is subject to quite large deflections in even a weak magnetic field. It was first hoped to overcome this by surrounding the whole electrometer with a large triple walled cylindrical iron shield, but while this reduced the effect it was still too great. The next step was the making of a much more intricate shield to go inside the case of the Hoffmann and completely surround the binants which contain the system. The sides and top were all protected by three shells of iron separated by two shells of brass, and the bottom by two shells of iron and one of brass. This assembly replaced the heavy copper shield originally surrounding the binants and looked very impressive, but failed to work. It seems quite reasonable to attribute its futility to the poor permeability of the inner shields in the weak fields to which they were exposed due to the successful working of the outer shield. Some such substance as permalloy having high permeability in weak fields, might prove more suitable for the inner members of such a system of shields. The failure of this system of shields caused the abandonment of the Hoffmann

for at this time it appeared that the low grid current pliotron, FP54, offered more hope of success, which is discussed in connection with the new apparatus.

In order to obtain the clearest graphical representation of the observed data, various methods have been tried. The plotting of electrometer deflections against magnet current was impracticable because sufficient precision was not attainable in the current readings. Although it presented some disadvantages the best arrangement seemed to be to plot in terms of some convenient parameter which could be easily read, and the settings of the rheostat used to control the magnet current were admirably adapted to this. The rheostat is wound with a hundred turns of wire and each turn is readily subdivided into a thousand parts, so small increments are easily read. A linear distribution of rheostat settings would be very convenient but it resulted in severe crowding of the peaks at one end of the scale and made interpolation very difficult because the distribution of molecular weight was according to an inverse square law. After a couple of unsuccessful approximations were tried a table of three hundred settings of the rheostat was worked out which, when spaced uniformly along the abscissa, would give a linear distribution of the square of the field and, hence, of the molecular weight. This table is reproduced in the upper panel of plate III. By varying the voltage of the magnet battery this table could be made to cover a wide range of desired dispersions without disturbing their

0	2 9226	7 1880	14 2900	23 4435
0415	9805	2769	4524	6417
0831	3 0385	3658	6148	8399
1250	0972	4562	7813	24 0482
1670	1559	5467	9478	2564
2094	2152	6386	15 1186	4757
2518	2746	7306	2894	6950
2946	3348	8241	4646	9261
3374	3950	9176	6398	25 1573
3806	4559	8 0128	8197	4016
4239	5169	1080	9997	6460
4676	5786	2048	16 1845	9047
5113	6404	3017	3693	26 1634
5554	7029	4002	5591	4379
5995	7654	4988	7489	7125
6441	8288	5990	9441	27 0046
6887	8922	6993	17 1393	2967
7338	9564	8015	3400	6083
7789	4 0206	9037	5408	9199
8244	0857	9 0077	7459	28 1249
8700	1509	1117	9539	5866
9160	2168	2177	18 1652	9386
9621	2827	3237	3337	29 3022
1 0086	3496	4316	4292	6812
0552	4165	5396	5262	30 0728
1022	4842	6496	6254	4818
1492	5520	7597	7247	9062
1967	6208	8718	8271	31 3472
2443	6896	9839	9295	8110
2924	7592	10 0983	19 0351	32 2920
3405	8289	2128	1408	7982
3891	8996	3294	2499	33 3272
4378	9704	4461	3590	8811
4869	5 0421	5650	4719	34 4621
5360	1138	6840	5848	35 0763
5857	1865	8053	7015	7203
6354	2593	9267	8182	36 4045
6856	3331	11 0506	9391	37 1245
7359	4069	1747	20 0600	8925
7867	4818	3011	1852	38 7055
8376	5567	4276	3105	39 5752
8890	6327	5569	4403	40 5012
9405	7088	6862	5701	41 4989
9925	7859	8182	7049	42 5669
20 446	8630	9502	8397	43 7274
0971	9414	12 0851	9798	44 9794
1497	6 0198	2200	21 1199	46 3507
2030	0993	3578	2655	47 8427
2563	1789	4957	4112	49 5012
3101	2597	6367	5628	51 3337
3640	3405	7778	7145	53 3827
4185	4225	9220	8725	55 6944
4730	5046	13 0663	22 0306	58 3303
5282	5880	2139	1955	61 3741
5834	6714	3615	3605	64 9429
6392	7561	5126	5328	69 2075
6950	8409	6637	7052	74 4282
7515	9269	8183	8855	81 0248
8081	7 0130	9730	23 0658	89 7329
8653	1005	14 1315	2546	101 9884



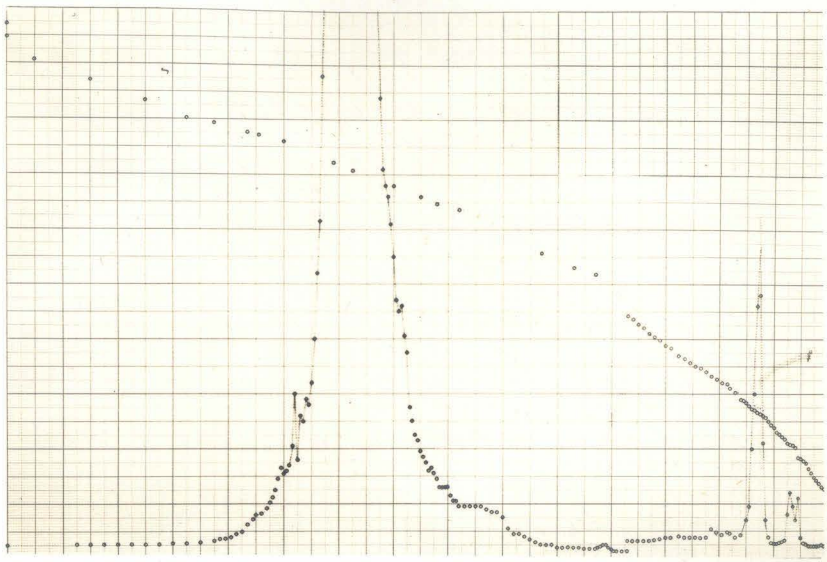
linearity. This permitted very convenient interpolation for the identification of peaks from their locations, but it was necessary that the same scale be preserved throughout the range. The latest and best arrangement for plotting is independent of the locations of the peaks along the abscissa for it makes use of a second curve plotted concurrently with the first which gives a continuous indication of the square of the magnetic field. Thus only the value of the ordinate of this curve is required for the identification of any peak since the relation between field and molecular weight is constant. The points for both curves are plotted as observed, for this is much less laborious than tabulating readings and plotting afterward. Also a point which deviates from the curve is immediately apparent and can be checked promptly, while it might be overlooked in the tabulation. The precision with which the points are read is best realized in the plotting by pricking them in with a fine needle, and the important regions of the curve are emphasised later by drawing a small circle about each point with a rivet pen.

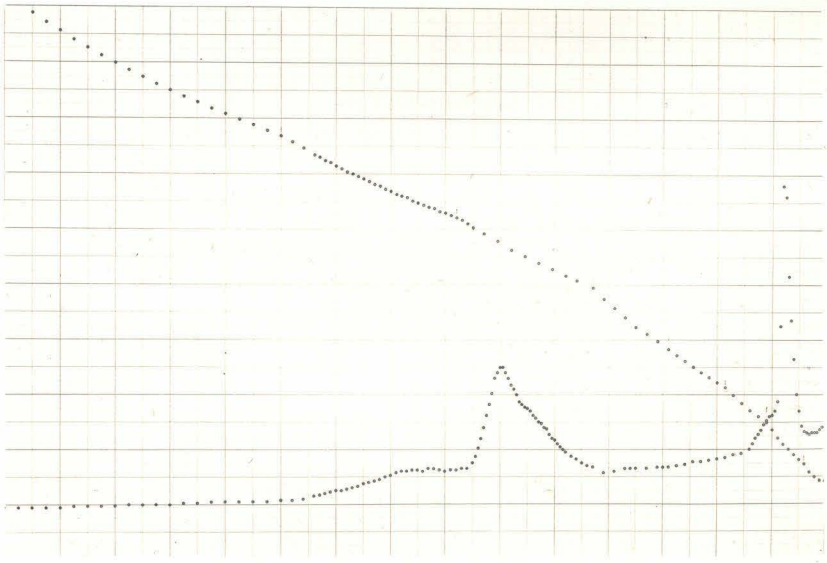
A representative selection of the results obtained is reproduced below; some of the curves showing the results obtained under favorable conditions and others showing the strange and sometimes inexplicable effects accompanying the results when conditions are adverse. The plates reproduced have been chosen to illustrate results under a variety of conditions rather than to show a complete study of any one substance.

Plate IV shows in the upper panel an early run on nitrogen bombarded with 90 volt electrons. The range of molecular weight covered is from roughly 300 down to almost zero, decreasing from left to right. These observations were made with the Hoffmann electrometer and are somewhat more irregular than those made with the pliotron circuit. The largest peak is about where Hg^{+} would be expected but the uncertainty of identification is such that it may represent either W^{+} or Th^{+} from the filament. When more certain identification became possible the large peak no longer appeared so the question was not settled. The sharp peak at the right is due to N_2^{+}, and the other to N^{+} or to N_2^{++} which is indistinguishable from it by this method. No real significance can be attached to the irregularities in the shapes of the various peaks. The upper curve on this sheet is a plot of the magnetic field as determined by a ballistic galvanometer.

The lower panel of plate IV shows a later run on

PLATE IV

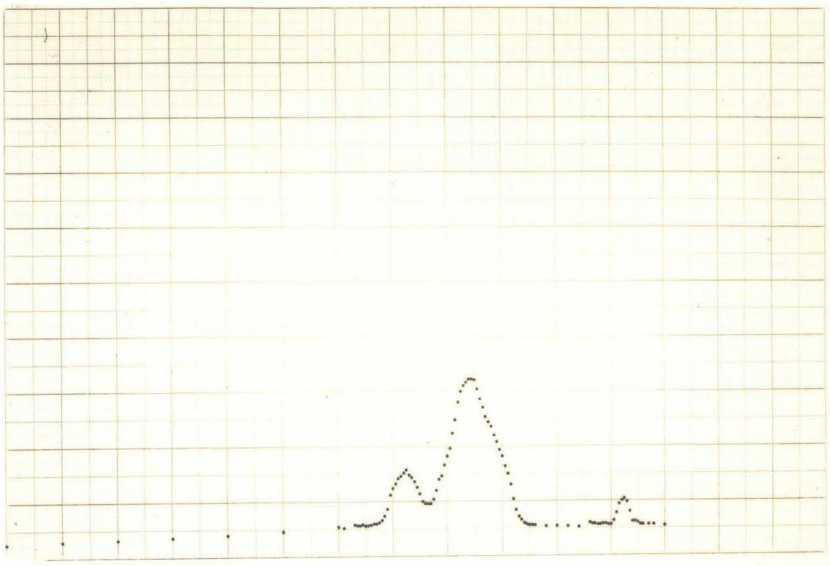


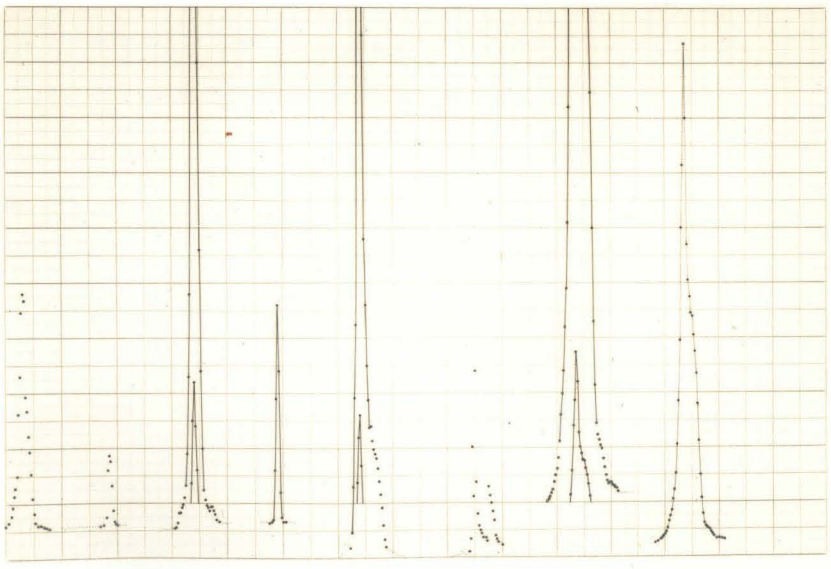


nitrogen bombarded with 65 volt electrons. Again an unidentified peak due to some heavy ion appears but it is definitely lighter and less intense in proportion to N_2^+. The run was not continued far enough to include the N^+ peak. The upper curve indicates the current in the magnet winding, the breaks being due to changes in the size of step taken with the rheostat in an effort to preserve approximately linear mass dispersion.

The upper panel of plate V shows still another run on nitrogen, this time bombarded with 40 volt electrons but the scale of molecular weights has been changed to include a much smaller region. The left hand peak is the familiar N_2^+ and the right is N^+ but the largest was for some time unexplained, although its weight appeared to be 23, agreeing with Na^+. Finally it was traced to some borax that had been used as a flux in silver soldering the grid. In the hope that this might serve as a source for other ions some magnesium borate was prepared and placed at the same point but no ions could be found.

The lower panel of plate V is reproduced to show the effect produced on the peaks when the focussing error was discovered and partially corrected, and should be compared with the upper panel. Although part of the region between the peaks has been deleted the scale is unchanged. The electron current has been increased somewhat but the resulting ionization is still not in proportion to the height of the peaks, the greater intensity being largely due to the improved location of the focal slit. The peaks are all taken in nitrogen,

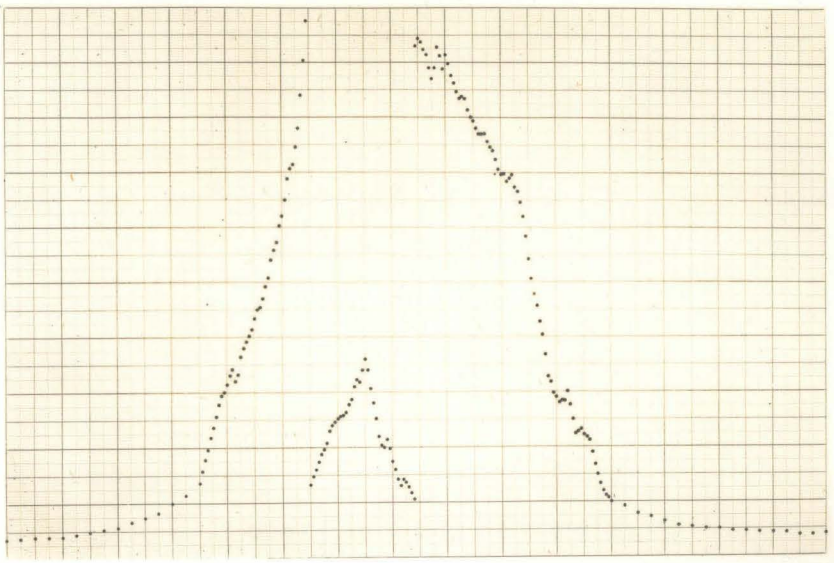


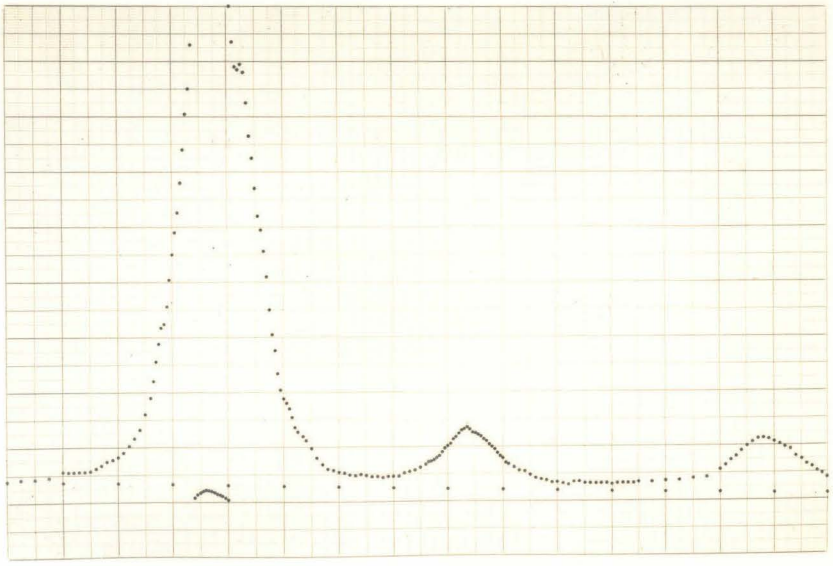


and in each pair the left hand one is due to N_2^+. The first pair were taken at 45 volts, the second at 113, and the third at 35 volts but in this pair the right hand peak was marred by the extinction of the discharge current. The left hand peak of the last group is the strongest of all and was taken with 60 volt bombardment but its high intensity is due to using more than twice the electron current previously employed. In each case the part of a peak lying off the top of the page is reduced ten times by shunting the galvanometer. The last peak on the sheet is the same as the next previous but has been condensed four times vertically so it can all be shown to the same scale.

The upper panel of plate VI shows one peak of an entirely similar run, but plotted to a horizontal scale fifteen times as great in order to examine the peak in more detail. Aside from verifying the pronounced asymmetry of the peak little added information was gained.

The lower panel of plate VI is included to show the degree of separation obtained for unit difference in molecular weight in the region 12, 13, 14. These peaks are due to N^+, CN^{++}, and C^+, and this sheet shows for the first time the really satisfactory method of identifying peaks made possible by the magnetic balance although here the problem of identification was quite simple. The deflections of the balance are plotted as a nearly straight line slightly below the base line of the peaks, and the ordinate of this line corresponding to the crest of a peak is proportional to the molecular weight of the peak.

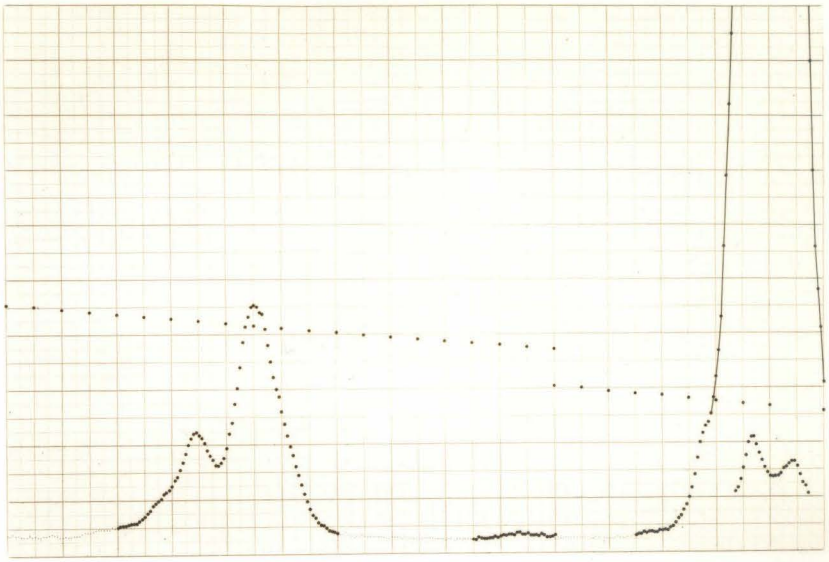


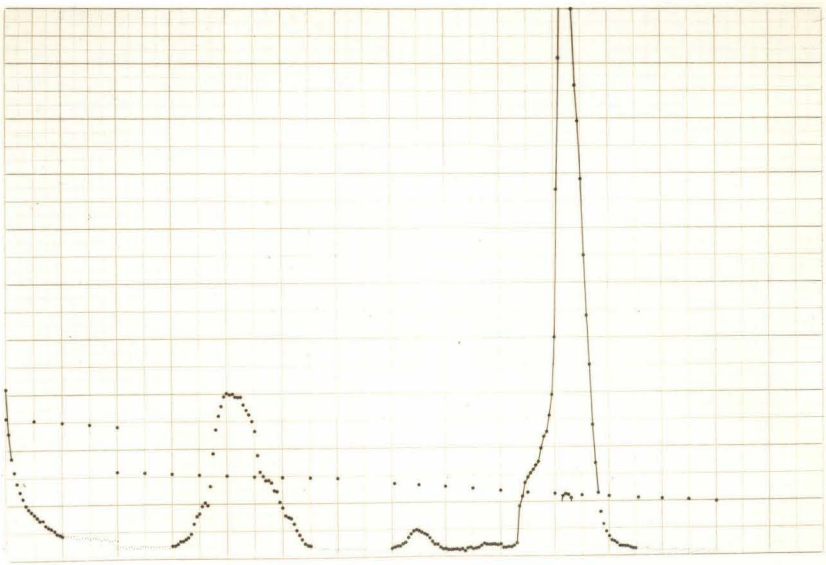


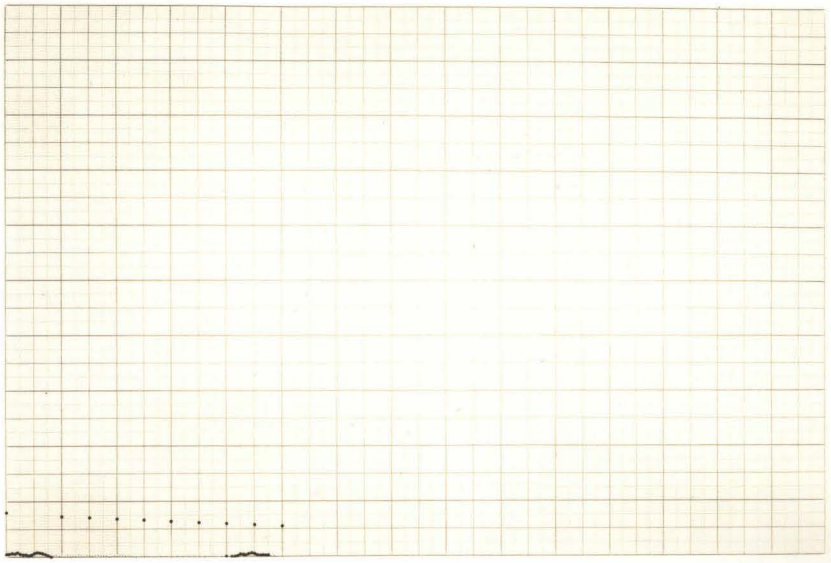
The next three panels, including all of plate VII and the upper one on plate VIII, belong to a single run in carbon monoxide at 132 volts, under conditions which permitted an arc discharge. In the first panel the left hand peak is bifurcated and the higher branch is due to CO_2^+ but the other branch is one unit heavier and has not been accounted for. The very weak peak is almost certainly due to C_2O^+. The higher branch of the right hand peak agrees very well with CO^+ but its companion is unexplained. The second panel shows in succession O^+, CO^{++}, and C^+, while the last shows faint but reliable indications of C^{++} and O^{++}.

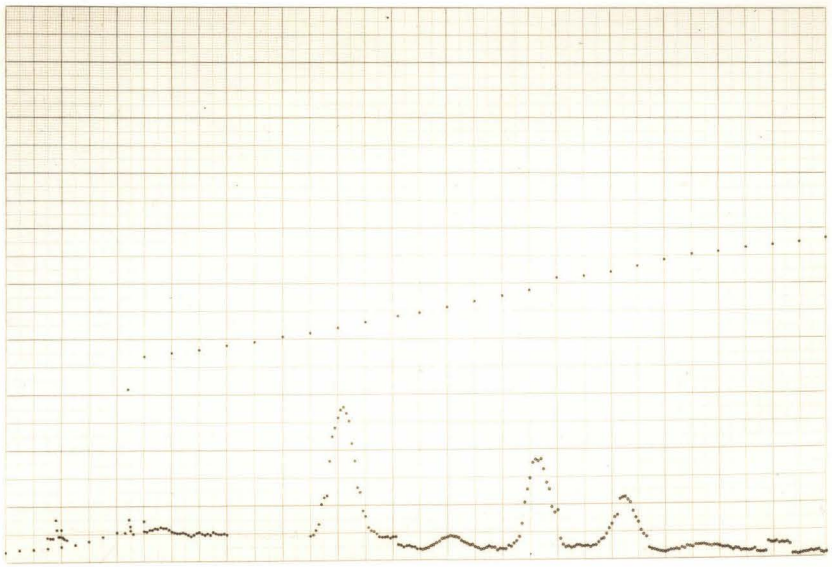
The lower panel of plate VIII shows part of a run on ammonia at 131 volts without arc discharge. If run in the usual direction the retentivity of the iron does not permit the field to fall low enough to focus the H^+ and H_2^+ peaks so this was made in the reverse direction. From the left the peaks shown are; H^+, H_2^+, N^+, NH^+, NH_2^+, NH_3^+, and NH_4^+. In all the work on ammonia the intensities of NH_2^+ and NH_3^+ are consistently comparable, with NH^+ and NH_4^+ being much weaker. There is no meaning to the break in the curve at the extreme right.

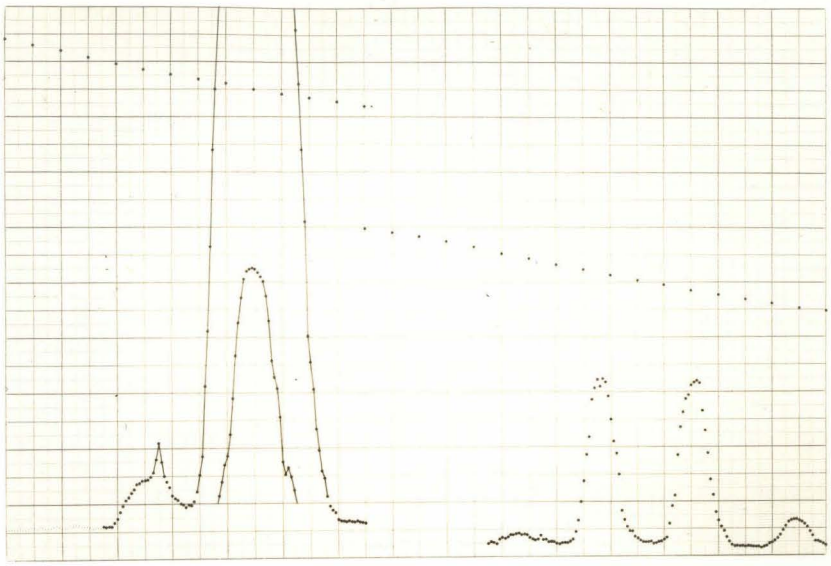
Plate IX shows a similar run on ammonia taken in the normal direction and shows very nicely the equality between NH_2^+ and NH_3^+. The large peak is due to N_2^+ and its companion may be due to N_2H^+ but this is uncertain.











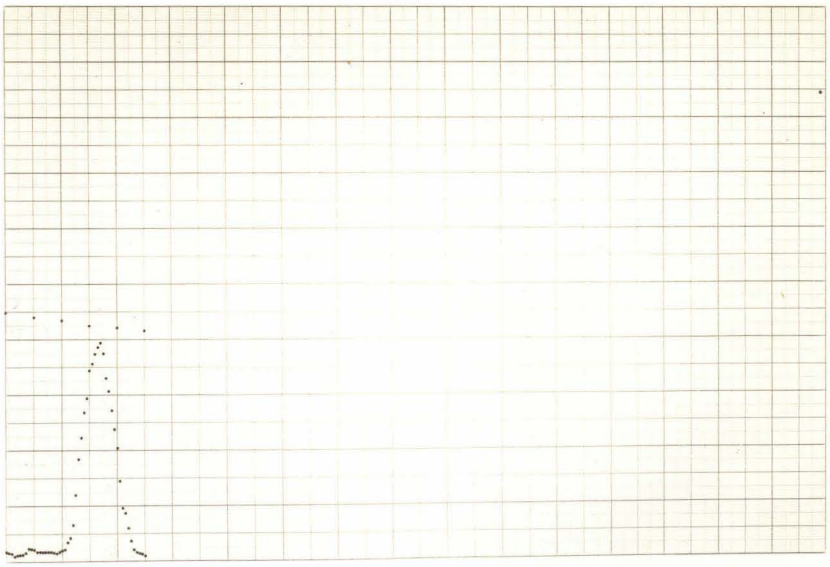
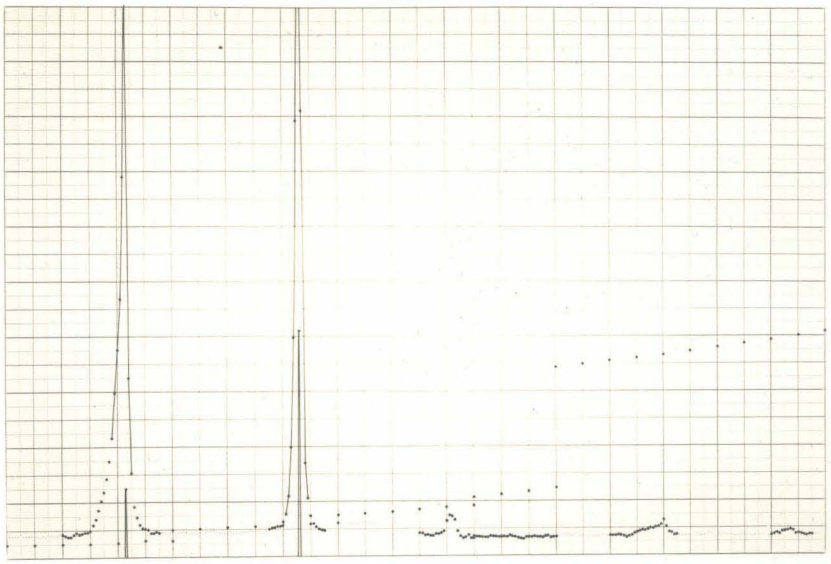
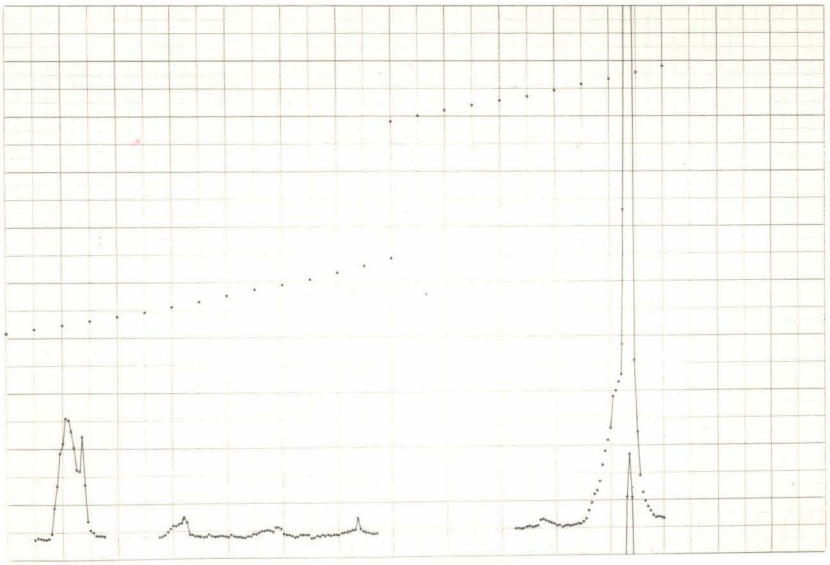
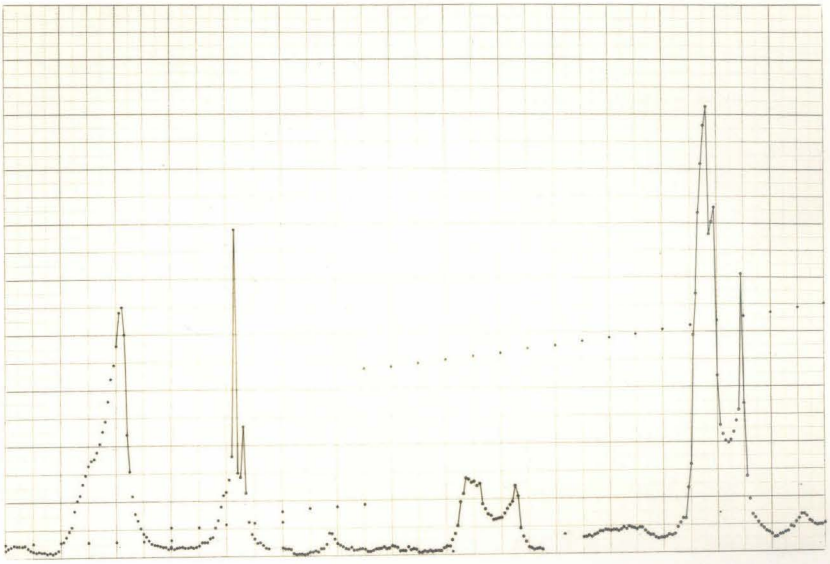


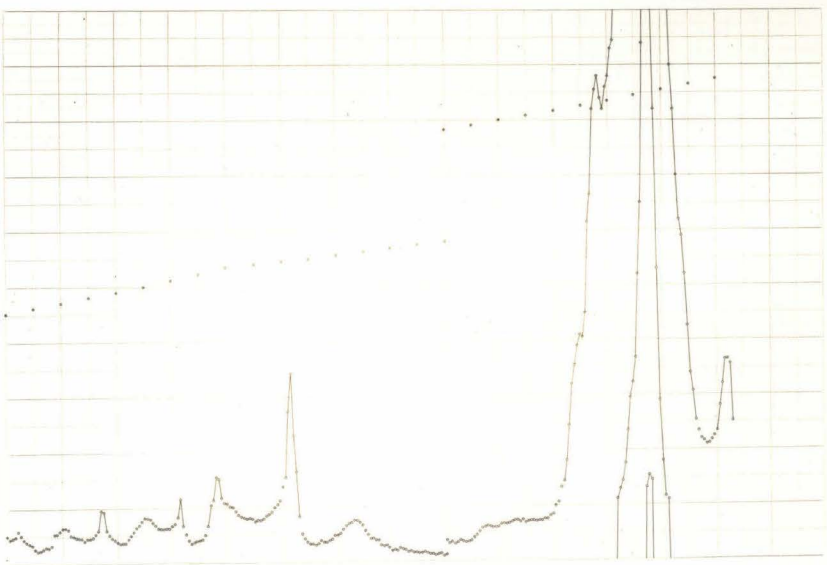
Plate X shows a run under arc conditions on a mixture of three parts hydrogen to one of nitrogen. The bombarding voltage was 80 volts. The peaks due to the pure components are quite strong but those corresponding to compounds are weak although still certain. The peaks shown are H^+, H_2^+, H_3^+, C^+, and CH^+ in the upper panel, with N^+, NH^+, NH_2^+, NH_3^+, and N_2^+ below. A faint companion to the left of N_2^+ is unexplained.

Plate XI shows a run in all ways closely similar to plate X except that the gas mixture is contaminated with some atmospheric air. However the results look entirely different for the peaks are in many instances twinned, greatly complicating the interpretation of the results. Although the positive ion current in this run is somewhat greater it is difficult to see how that can be responsible for the effects found. It is hoped the new apparatus can shed some light on this by the elimination of focussing error.









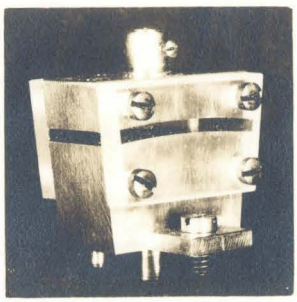
Although the old apparatus failed completely only in the error in focussing due to the wrong shape of the pole faces, it seemed impracticable to correct that error and use the rest of the existing apparatus. The whole apparatus was assembled with soft solder and in spite of careful use of liquid air traps the solder had become impregnated with mercury from the pumping system so that the mechanical strength of the joints was very low and vacuum leaks were prevented only by the free use of Glyptal varnish. Also the homogeneity of the field between the pole faces was not satisfactory, and various additional improvements were of sufficient importance to warrant complete rebuilding.

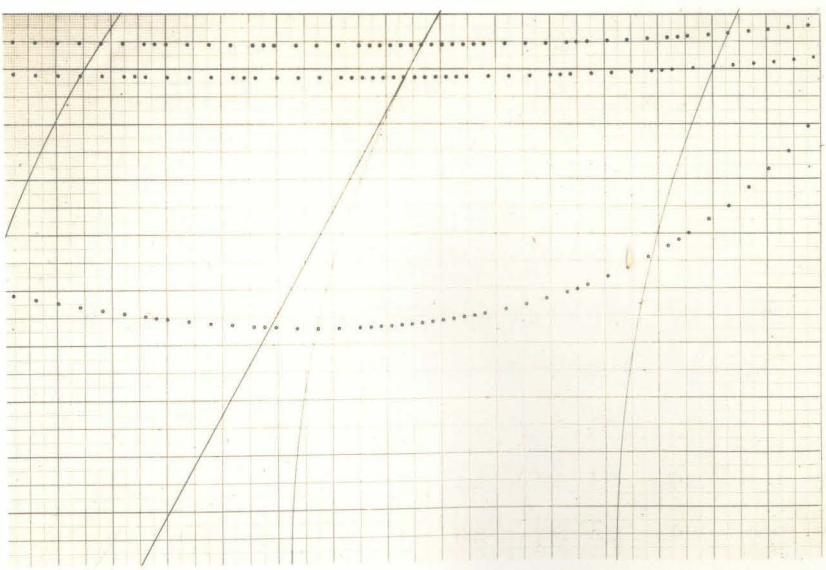
The only important change in the method of producing the ions is the substitution of an equipotential type emitter for the old tungsten filament in order to have the bombarding electrons of more nearly uniform energy. Considerable difficulty has also been experienced from the bursting of the outer shell of the large ground joint carrying the filament assembly. This was due to the fact that the glassblowing equipment was inadequate for working the necessary amount of pyrex for a shell of the proper thickness. This difficulty has been overcome by making the ionization chamber and the shell of the ground joint of steel, using silver solder for assembling the parts. The grinding of the ground joint is somewhat more difficult with this construction

but this is more than offset by its advantages.

A slight modification in the measurement of current in the high potential circuit has been introduced to eliminate the effect of leakage currents. A perforated graphite disk is supported in front of the collimator and is suitably insulated so that the current received on it can be measured and leakage currents will not pass through the microammeter.

In Aston's apparatus the plates of the electric deflecting field are flat and parallel and inclined at the same angle to both the incident and emergent median ray. This arrangement has the very useful property that the backward prolongations of the emergent rays will all pass through a single point, and this point is quite convenient in the consideration of the magnetic field. However when the electric deflection is increased to one quarter radian the necessary separation of flat parallel plates becomes excessive, requiring higher voltage to produce the same field and exaggerating the edge effects of the field. Since these edge effects are of unknown magnitude and can not be calculated readily it was considered advisable to substitute for the flat plates equiangular sectors of coaxial cylinders which would permit much closer spacing. These plates are made of brass, gold plated to prevent corrosion, and are held a fixed distance apart by spacers of glass fixed to each side by screws. The lower plate is in electrical contact with the body of the apparatus





and is accurately located by dowels so it may be removed and replaced readily. A photograph of the electric field assembly is reproduced in the upper panel of plate XII.

Neglecting edge effects the field between the two plates is an inverse first power field and the solution of the motion of a charged particle in such a field is of a very involved nature but has recently been worked out for the case required here. (See Doctor's Dissertation, G. C. Munro, California Institute, 1933)

All the rays are assumed to be parallel and to enter the field at the same point, on the leading edge midway between the plates. It is required to find the emergent paths and velocities, for the velocity determines the radius of curvature in the magnetic field and the emergent path determines the point of incidence to the magnetic field. The emergent path is described by the angle it makes with the median ray and the point at which it cuts the trailing edge of the electric field.

All solutions are given in terms of a parameter,

$$\varkappa = \Phi_0 / 2E \lg(\rho_2/\rho_1)$$

Φ_0 is the voltage applied to the electric field, E is the energy of the particle in electron-volts and ρ_2 and ρ_1 are the outer and inner radii of the electric field. If the center of curvature of the plates of the field be taken as the origin, the median ray describes a circular arc of radius α about this point and the radius to the point of emergence of any ray is $\rho = u\alpha$. u is one of the characteristic quantities of the emergent path and is given by $u = 1 + (1-\varkappa) \cdot f(\varkappa)$. The other character-

istic quantity of the emergent path is the tangent of the angle between the emergent ray and the median ray, and is expressed by $(1-\varkappa)\cdot F(\varkappa)$. A positive sign for this quantity indicates that the ray undergoes a greater deflection in the electric field than does the median ray.

The relation between the emergent velocity V and the incident velocity v is expressed by

$$V=v\sqrt{[1-\varkappa(1-\varkappa)\cdot\Phi(\varkappa)]}$$

The series involved in these expressions are:

$$f(\varkappa)=.032,085,023,984,212$$
$$-.001,204,289,203\varkappa+.000,046,880,55\varkappa^2-.000,001,853,96\varkappa^3$$
$$+.000,000,073,95\varkappa^4-.000,000,002,97\varkappa^5+.000,000,000,11\varkappa^6$$

$$F(\varkappa)=.255,341,921,221,138$$
$$-.010,957,952,9\ \varkappa+.000,458,419,9\ \varkappa^2-.000,019,040,1\ \varkappa^3$$
$$+.000,000,790,8\ \varkappa^4-.000,000,032,5\ \varkappa^5+.000,000,001,3\ \varkappa^6$$

$$\Phi(\varkappa)=.031,581,051,247,468$$
$$-.000,673,377,81\varkappa+.000,018,721,99\varkappa^2-.000,000,627,57\varkappa^3$$
$$+.000,000,019,2\ \varkappa^4-.000,000,000,65\varkappa^5+.000,000,000,02\varkappa^6$$

The parameter $\varkappa$ has the value unity for the median ray, is less than unity for rays of greater energy, and is greater than unity for rays of less energy. It was considered advisable to extend the calculations over the range $\varkappa=0.5$ to $\varkappa=1.5$ to aid in defining the bounding curve of the magnetic field even though the usable part of the field is included in the range $\varkappa=0.7$ to 1.3

It can also be shown from these results that while the backward prolongations of the emergent rays do not pass exactly through a single point, it is a very satisfactory approximation to assume that they do for each

ray intersects every other within a very small region.

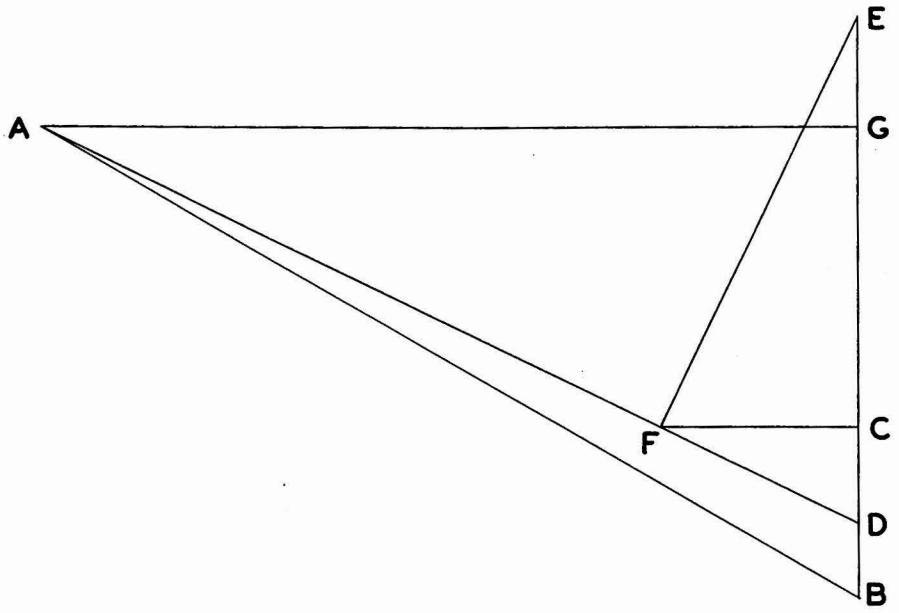
In connection with the complete redesigning of the apparatus it seemed advisable to investigate whether better results might not be possible with some different ratio of magnetic to electric deflection. The same electric deflection that had been previously used, one quarter radian, was again chosen and five different values of magnetic deflection were combined with it in a graphical solution in order to examine the resulting mass dispersion. The cases selected were for deflections of one-half and one radian in the same direction as the electric deflection, and one-half, one, and $\pi/2$ radians in the opposite direction. The case previously used, one radian in the reverse direction, was found to be best for no other case gave any better dispersion and most required shapes of the magnetic field much more difficult to construct. The desirable restrictions on the shape of the magnetic field are; the incident rays should be approximately normally incident and the angle of incidence should have only a small variation over the usable range of the pole face, and the bounding curve of the pole face should preferably be one that can be generated mechanically, or at least one of small and regular curvature so that it can be cut with reasonable precision on ordinary machine tools.

Considerable importance is also attached to the proper selection of material for the magnetic circuit since so much depends on the homogeneity of the field. There seem to be only about three suitable materials

for a large magnet; Armco iron, Swedish or Norway iron, and Rema iron. In the present instance neither Norway nor Armco was available in the required size so the selection of Rema was indicated. Fortunately it is also probably the best of the three. An average analysis of Rema dead soft electric furnace charcoal iron, kindly supplied by the local agent, gives the following limits for impurities: Carbon, .02-.05%; Manganese, .2-.7%; Phosphorus, .002-.005%; Sulphur, .015-.020%; and Silicon, .15-.25%. Since this iron was available only in a very wasteful form the local agent, Ryer, Inc., had the necessary amount forged from a six inch Gothic ingot to a four inch square section. Through the courtesy of Mr. D S Clark a metallographic examination was made of a specimen as received and again after thorough normalization and this revealed that no advantage would result from further annealling so the iron was used as received. Although quite soft it works extremely well and seems completely homogeneous, apparently an admirable material for magnetic work.

Since the analysis of the electric field had shown that no analytic expression existed for the characteristics of the beam after traversing the electric field, the only available method for determining the proper shape for the magnetic field lay in assigning appropriate values to the parameter κ and so calculating a series of points on the desired curve. It was found that the calculation could be greatly simplified by introducing the further restriction on the magnetic field that it be symmetrical with respect to the perpendicu-

lar bisector of the line joining the focus to the point in the electric field which is assumed to be a virtual source for the emergent rays. This conveniently locates the center of curvature for any ray on this axis of symmetry. The necessary geometrical considerations



are shown in the figure in which BE is the axis of symmetry, and A the virtual source in the electric field. AD is a ray which makes an angle α with the median ray AB, and since $\angle BAG=\frac{1}{2}$ radian, $\angle$s FEC, DFC, and DAG are each equal to $\frac{1}{2}-\alpha$. EF$\perp$AD and is of length R, and FC$\perp$BE B is taken as the origin of a system of rectangular coordinates with x positive upward and y for convenience positive to the left. $y=FC=R\sin(\frac{1}{2}-\alpha)$; $x=BC=BD+DC=AB\sin\alpha\sec(\frac{1}{2}-\alpha)+R\sin(\frac{1}{2}-\alpha)\tan(\frac{1}{2}-\alpha)$. All needed quantities are known with the exception of R which is given by the relation $R=R_0\sqrt{[1/\kappa-2(1-\kappa)\cdot\Phi(\kappa)]}$ in which R_0 is the radius of curvature of the median ray in the mag-

netic field. Such a calculation was used to determine the x and y coordinates of fiftyfive points on the edge of the magnetic field, and the lower panel of plate XII shows a plot of these points. The upper curve shows the original points plotted to five times full size in each dimension and the lower curve is times five on the abscissas and times fifty on the ordinates to check the smoothness of the curve. The intermediate curve shows the same points after the edge correction had been applied.

The original points were based on the assumption that the magnetic field between the pole faces is uniform and everywhere else is zero, but unfortunately the actual situation is different. The effect of the edge is to weaken the field somewhat near the edge inside, and the field also fringes into the space outside the poles. This required the computation of two edge corrections, which was done by Mr. Munro. (See reference above) The results obtained show that to a reasonable approximation the line integral of the magnetic field along the path of a particle when calculated by means of a Schwartz transformation is the same as if the uniform field were taken to extend beyond the edge a distance equal to eight-sevenths of the air gap. However it must be noted that all rays do not have the same angle of incidence so the correction must be modified accordingly. This is now sufficient to determine the final form of the edge but the points as determined by the parameter $\varkappa$ do not represent equal increments in x

and would be inconvenient to set up in actually cutting the shape of the face. For this reason the origin of coordinates was shifted to lie in the bottom edge of the pole face and an interpolation was made for a new series of points lying uniformly 0.040 inch apart in the x direction. An attempt was made to approximate the curve by means of an ellipse which could be generated in the milling machine, but when a general conic was fitted to the points by the method of least squares it proved to be a hyperbola having an eccentricity far removed from a possible ellipse. The actual points are:

x	y	x	y	x	y	x	y
0.000	1.7889	1.000	1.7714	2.000	1.7703	3.000	1.8084
040	7881		7709		7709		8114
080	7873		7704		7714		8145
120	7865		7700		7722		8179
160	7857		7696		7729		8213
200	7849		7693		7738		8249
240	7841		7691		7746		8288
280	7832		7688		7756		8328
320	7824		7685		7765		8368
360	7816		7683		7775		8408
400	7808		7681		7788		8458
440	7801		7680		7800		8510
480	7794		7679		7813		8563
520	7786		7678		7828		8615
560	7779		7677		7844		8668
600	7771		7677		7858		8720
640	7765		7678		7877		8773
680	7758		7679		7895		8825
720	7752		7680		7915		8878
760	7745		7682		7935		8930
800	7740		7684		7956		8983
840	7734		7687		7978		9035
880	7728		7690		8005		9088
920	7722		7694		8029		
0.960	7718		7698		8055		

The actual cutting was done on the shaper, utilizing a long stroke indicator on the feed motion and a regular indicator for the depth of cut. Whenever the

feed indicator pointed to a multiple of 0.040 the depth of cut was quickly adjusted to the right value for that point, so that a series of steps was cut whose envelope was the desired curve. The final finish was obtained by scraping by hand until the tool marks were just visible. It seems likely that a precision of 0.001 or at most 0.002 inch should be realized by this means.

When it was finally decided to use the FP54 pliotron in place of the Hoffmann there happened to be one already on hand so it was quickly tried out in a one tube circuit, although it was hardly reasonable to expect one tube to be sufficient. This showed that it would be necessary to use a two tube circuit in order to combine sufficient stability with the required sensitivity. However when the second tube was obtained so great was the disparity between it and the first that the usual circuit would not permit compensation for the difference, but a determination of the complete tube characteristics showed that a slight modification would suffice. As originally set up the circuit included several radio potentiometers and variable resistances which were a continual source of trouble because of the poor contact between the rotating arm and the winding. Increasing the contact pressure frequently resulted in displacing the winding, thereby making matters still worse. The trouble was finally eliminated by substituting soldered connections wherever possible, and devising a new type of potentiometer for the necessary adjustments.

The present form of the circuit is shown in the upper panel of plate XIII. The upper portion of the drawing represents the part of the circuit which is included within the mass-spectrometer, while the lower part shows the arrangement of the control box. The five long horizontal lines in the control box constitute the main potentiometer, the current through which supplies all the potentials for the tubes. This potentiometer consists of five long strands of a composite resistance wire having a total resistance in series of about 80ω. This wire consists of a black enamelled copper core overlaid with a serving of asbestos fiber, on which in turn is wound the actual resistance wire. This successfully avoids the necessity for using small and fragile wire sizes or inconvenient lengths to obtain the necessary resistance. This wire is regularly used in certain types of Electrad resistors and was obtained from one of them. Contact with the wire is made with Eby Midget binding posts which are so made as to permit firm contact with no danger of cutting the wire. The circuit battery consists of 18 volts of 100 ampere hour Exide radio batteries and supplies quite constant voltage, needing to be charged about once in two weeks. The potentiometer is seen to be broken near the left end of the second strand and this gap is bridged by the filaments of the two tubes, so that the potentiometer current is the sum of the filament currents for both. Because of the difference in filament characteristics some additional resistance is included in series with the filament of the dummy tube. R_1 is a 20ω variable

resistance for fine control of the potentiometer current. R_2 is a 2000ω variable resistance for fine adjustment of the galvanometer zero by slightly shifting the space charge grid potential of the second tube. R_3 and R_4 are 25000ω wire wound fixed resistances, which, with the plate impedances of the tubes, form the bridge across which the galvanometer is connected. R_5 is a 100000ω wire wound resistor in parallel with the plate impedance of tube 2 to bring it to equality with that of tube 1. R_6, $1.3\times10^{12}\omega$, and R_7, $5.3\times10^{11}\omega$, are high resistance shunts from the S. S. White Co.

The balancing of this circuit is rather less convenient than for a circuit containing more variables, but its real advantage lies in the fact that rebalancing is less often required for there are fewer contacts subject to spontaneous variation. The most convenient method is the use of the tube characteristics, particularly the curves of plate current vs plate voltage and plate current vs filament voltage. The proper potentiometer settings for the positive filament terminals are determined from the filament voltage characteristic and the proper value of the plate shunt is obtained by comparison of the plate impedances. Then the control grid and plate potentials are set at their recommended values, due allowance being made for the voltage drop through R_3 and R_4. If the space charge grid potentials are set at their recommended values the plate currents may be decidedly unequal so one or both must be shifted to obtain this equality. Then by the use of a galvanometer and Ayrton shunt the final balance is obtained

by further variation of the space charge grids, the final steps being made on R_2.

The very best electrical shielding of all parts of the circuit is of the greatest importance in order to secure stable operation. The storage battery is placed in a copper sheathed box surrounded by a double walled celotex box for temperature control, although there is some doubt now if temperature variations are as serious as they were once thought. All control devices are contained in a box sheathed inside and out with copper. The pliotrons and their high resistances are mounted in high vacuum inside of the mass-spectrometer, and thus fully protected against moisture, and picking up of atmospheric ions and also electrical disturbances. This also obviates the necessity for bringing out a highly insulated electrometer lead with its resulting added capacity. All leads are also well shielded, but flexible metal gas tubing which was first tried proved to be worthless against high frequency disturbances so a tubular copper braid made by the Roebling company was substituted with good results. A special ground connection is provided outside the building and a heavy shielded lead connects it with the circuit at the common negative filament terminal, while the shield around the ground lead is used as the ground connection for all other shields. It was also found advantageous to jacket the cylindrical portion of the tubes with nickel gauze which is connected to the control grid lead behind the shunt as shown.

Many different types of high resistance shunts

were tried such as india ink line on bristol board, the same impregnated under vacuum with paraffin or ceresin, alcohol-xylol mixtures in sealed glass cells with platinum electrodes, rods made of granulated carbon with an organic binder, and pencil line on amber. These all had to be abandoned for various reasons; some were too variable, others were too hard to adjust, introduced too much capacity, exhibited polarization etc. Finally a satisfactory solution was found in the use of molded composition resistors secured from the S S White Dental Manufacturing Co., 152 West 42nd St., New York. No attempt has been made to check the constancy or the value of the resistance, but the fact that they permit stable operation at a sensitivity of 2×10^{-17} amperes per scale division is taken as sufficient indication of their suitability for this work.

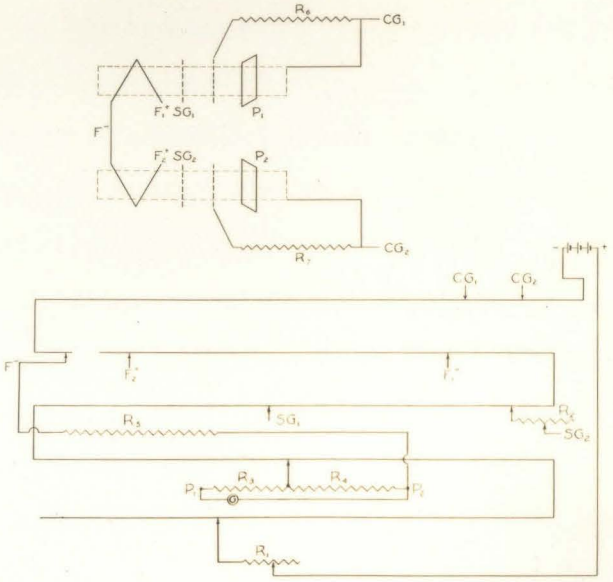
Certain special features have been incorporated in the new apparatus to fill needs that have arisen in the operation of the old apparatus. These are described below to indicate their probable usefulness.

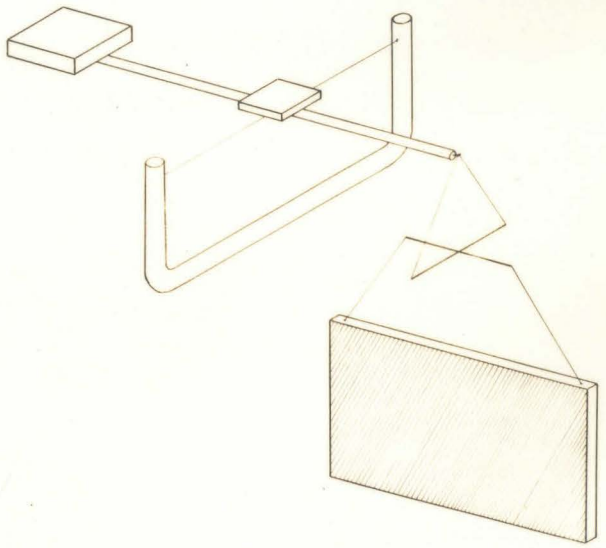
A shutter system has been introduced into the beam just ahead of the magnetic field so that a slit of variable width may be placed at any desired position in the beam, with both the width and the position controllable from outside through a double cone joint. This will permit the analysis of the various ion peaks in terms of the energy of the component particles and it will be very interesting to learn if certain ions are produced at such a location in the discharge that their

energies are significantly different from the maximum available. Also the shutters will permit a test of the correctness of the form of the pole faces by investigating whether all zones of the magnet focus at the same point. If certain regions are in error it will also be possible to eliminate their effect by intercepting their contribution with the shutters, making good results possible from the remainder.

Previously when new peaks were being sought for the first time, as when a new substance had been introduced or instrument adjustments changed, it was quite a laborious job to find the approximate locations, for a great many points had to be taken close together in order not to overlook a peak. In the new apparatus the focal slit is double and either of two sizes of slits can be selected by an external adjustment. Thus the broad slit is used for determining approximate locations of peaks, when the narrow slit is substituted for their analysis. There is also the possibility of complete closing of the slit when it is desired to check the zero of the pliotron circuit. A photograph of the slit is shown in the upper panel of plate XIV.

To permit obtaining the best focus a radial motion of the entire collector system is provided for by using a sylphon connection between the collector system and the body of the instrument. Also a tangential motion is permitted by hinges opposite the sylphon in the rods supporting the collector system, and a micrometer tangent screw varies the inclination. Thus with the magnetic field fixed the same peak may be repeatedly plot-


R6
CG1
F1+ SG1
P1
F−
F2+ SG2
P2
CG2
R7
CG1
CG2
F−
F2+
F1−
R5
SG1
R8
SG2
R3
R4
P1
P2
R1



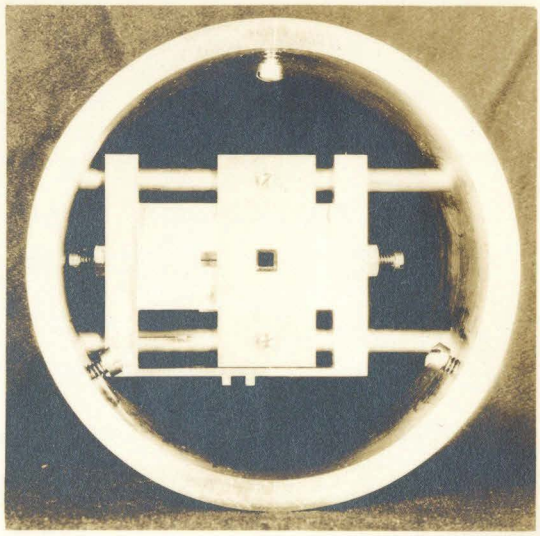
ted under varied conditions by using the tangent screw.

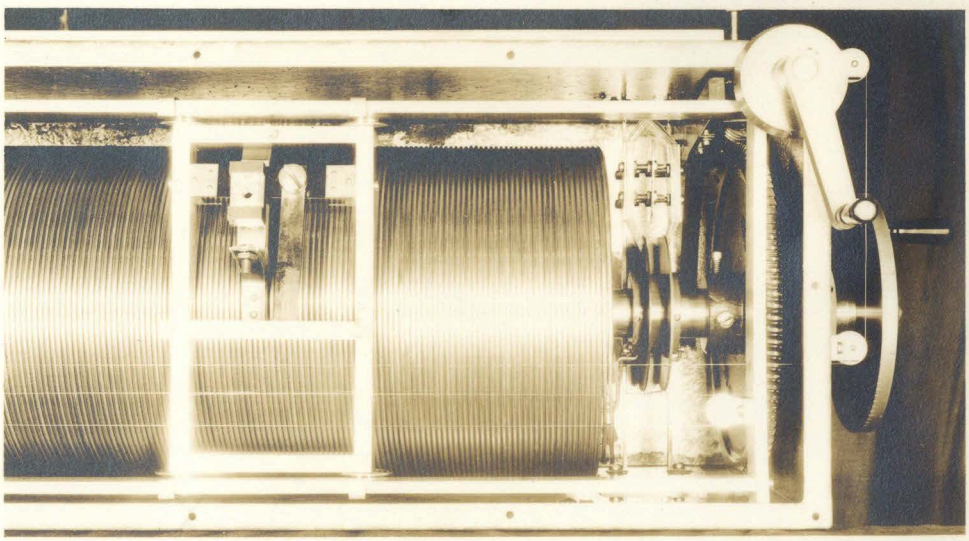
An entirely unexpected development from another research in this laboratory was a simple and elegant means of obtaining a continuous indication of the field strength in the air gap. The method is an inverse application of the Gouy method of measuring diamagnetic susceptibilities. In brief the Gouy method consists in suspending a cylinder of diamagnetic substance having its axis vertical so that one end is in a region of uniform field and the other is in zero field. Force exerted on the specimen by the field is then measured and this force is proportional to the susceptibility of the substance and to the square of the field strength. Thus by using a substance of known susceptibility the force is proportional to the square of the field. In order to obtain good sensitivity a substance of high susceptibility is used, and pseudo-crystalline graphite has proved very satisfactory. This is prepared by allowing flake graphite to settle through a suitable medium so that the flakes are all oriented parallel. A slab of this material is suspended from a torsion balance which by means of a suitable optical system indicates on a scale the square of the field. Since the molecular weight of a peak is also proportional to the square of the field this can be calibrated directly in terms of molecular weight. To avoid mechanical hysteresis the torsion fiber is made of fused quartz, and the whole device is mounted inside the vacuum. A similar device mounted in an external air gap has been entirely satisfactory on the old apparatus. An isometric

sketch of the magnetic balance is shown in the lower panel of plate XIII.

In order to obtain sufficiently close control of the current through the electromagnet, it was necessary to design and build a large rheostat of a very special type. It was desired to be able to cover the whole range from minimum to maximum field with continuous variation of current because any system of steps would involve trouble with magnetic hysteresis. A partial view of the completed rheostat is shown in the lower panel of plate XIV. The main feature of the construction is the brass drum twenty six inches long and eight and a fourth inches in diameter, over the whole length of which is cut a specially shaped double thread of one quarter inch pitch. Two number ten gauge resistance wires are wound side by side in this thread and insulated from the drum by a layer of varnished cambric.

In order to obtain the desired resistance characteristic it was necessary to make the first eighteen turns of each wire of Advance, and the remainder of Nichrome, the joints being silver soldered. The free Advance ends are connected to collector rings as shown, with which connection is made through laminated bronze brushes, and the other ends are anchored separately to an insulating block so tests for short circuits and for grounds may be made. Mercury cups were originally installed on the collector rings instead of brushes but almost caused the loss of the rheostat for even the agitation of the mercury by the rings was sufficient to cause it to emulsify with the oil, thereby threatening





the amalgamation of the whole instrument. The wires are short circuited at any desired point by a wedge of copper mounted on the carriage which is capable of motion along the rails parallel with the axis of the cylinder. This wedge is sufficient to drive the carriage so that it follows the wire but it showed a slight tendency to lose contact with one wire so a laminated contact was added and the combination is entirely satisfactory. The minimum resistance obtainable between the terminals is less than one tenth ohm and the maximum is about twenty two ohms. A dial graduated in 100 divisions is mounted on the shaft and a slow motion gear of ratio 100:1 permits settings to .0001 revolution of the drum. In order to keep the surface of the wire clean the drum and carriage are immersed in transformer oil, which also practically eliminates temperature changes because the thermal capacity of the rheostat is enormous compared with the energy dissipated in it.

It is indeed a pleasure to acknowledge here the constant interest displayed by Professor Millikan in this problem. Special thanks are also extended to Dr. Smythe, who willingly assisted in overcoming many of the difficulties encountered and who kindly criticized the plans for the new apparatus. Much credit is also due the staff of the instrument shop for their skillful assistance in building apparatus, and to Mr. Clancy who has exerted his ingenuity to good purpose in my behalf on many occasions.