VIII. *Aluminium Cell.*

To show phaseograms by more irregular currents, I have made some experiments with an aluminium cell consisting of an aluminium wire against sheets of lead in dilute sulphuric acid (accumulator acid).

The three phaseograms show the cell in various stages: fig. 16 soon after the closing of the current; fig. 17 when the current has passed for a while; lastly fig. 18 shows an inactive cell (Pl. XIX.).

CX. *The Positive Thermions emitted by the Alkali Sulphates.*

By O. W. RICHARDSON, M.A., D.Sc., *Professor of Physics, Princeton University*.*

[Plate XX.]

EXPERIMENTS by the author † and Mr. Hulbirt ‡ have shown that the bulk of the positive thermions emitted by the commoner conductors, which can be heated to a sufficiently high temperature, possess very nearly the same value of e/m : a value which corresponds to a molecular weight m for the ions of about 25, on the assumption that they carry the same charge as the atom of hydrogen in electrolysis. There are a number of different ways in which it might happen that the various substances investigated might give rise to ions having the same specific charge, and these are discussed at length in the papers referred to. One of these views, and the one which seemed to have the most evidence in its favour, was that the ions consisted of atoms of sodium which were present as a common impurity in all the substances investigated. This view is supported among other things by the well-known fact that sodium compounds are very widely distributed, and by the fact that the value of m for the ions is very close to the atomic weight of sodium (23.05).

It was this view that suggested the present investigation. For it was felt, since the alkali metals and their compounds are so similar to one another in both chemical and physical properties, that if sodium compounds gave rise to positive ions having a certain specific charge, it ought to be possible to obtain ions having other values of e/m by substituting salts of the other alkali metals for those of sodium. The author therefore decided to measure the value of e/m for the positive ions emitted by the sulphates of the different alkali metals when heated.

* Communicated by the Author.

† Phil. Mag. [6] vol. xvi. p. 740 (1908).

‡ Phil. Mag. [6] vol. xx. p. 545 (1910).

The method adopted consists in measuring the deflexion of the path of the ions, between two parallel plates at different potentials, produced by a known transverse magnetic field. It was, in fact, the same as that used in the investigation of the specific charge of the ions emitted by hot bodies. So that, for the description of the apparatus and the method of using it, it will be sufficient to refer to the first of the two papers mentioned, which contains a very full account of the matter.

The experiments were carried out in the following manner : a strip of platinum 0.5 cm. long, .002 cm. thick, and about .05 cm. wide, was mounted in the apparatus. The distribution of the ionization over a parallel plate about .5 cm. away was then determined in the usual manner, with oppositely directed magnetic fields of about 4700 lines per cm. From the displacement of the maximum the value of e/m for the positive ions from platinum could be calculated.

After the measurement had been made, the platinum was strongly heated for several hours until it gave only a negligible leak at the temperature at which the test was made. The apparatus was then taken down, and a layer of the pure alkali salt to be tested was melted over the front surface of the strip. The apparatus was again set up and exhausted. It was now found that a large positive ionization could be obtained at a temperature below that at which the test on the platinum had been made, showing that the ionization was due to the alkali salt and not to the platinum. The distribution of the ionization on the opposite plate was now determined with the magnetic field in opposite directions, and the displacement of the maximum measured.

From this displacement together with the distance and difference of potential between the plates and the strength of the field the values of e/m and of m could be calculated from

the formula : $e/m = \frac{9}{2} \cdot \frac{Vx^2}{H^2z}$. In calculating the value of m

the ions were assumed to carry the same charge as an atom of hydrogen in electrolysis, and the value of e/m for the hydrogen ions in electrolysis was taken to be 9.66×10^3 E.M. units. In the present case we have a valuable check on the results thus obtained, on account of the simultaneous measurements which were made of the displacement in the case of the ions from platinum. Previous work has shown that the value of e/m for the positive ions emitted by this metal* does not vary much for different

* Richardson & Hulbirt, *loc. cit.*

specimens of the metal. By assuming the ions from platinum to have the average value (25.5) previously found, it was possible to calculate the values of e/m and m for the salts investigated without making use of the linear dimensions of the apparatus. If we could rely on the constancy of e/m for the positive ions from platinum, we could in this way get rid of the uncertainty arising from the difficulty of knowing the distance between the hot strip and the plates accurately. It is probable, however, that the value of e/m for the positive ions from platinum is only approximately constant, so that this method can only be regarded as a check on the other. The disagreement between the two methods was not much greater than the errors of experiment.

It has already been pointed out that the method is liable to an error on account of the uncertainty as to the position of the strip when heated. On account of the expansion and consequent curvature of the strip, this is not the same as when it is cold. This uncertainty was avoided in the former experiments by using the apparatus to measure the known value of e/m for the negative electrons. Assuming that the measurements would be liable to the same error whatever the sign or mass of ions, this enables us to determine a correction to be applied to the positive ions,

In the present investigation this procedure has not been followed. The distances z which have been measured are those between the back of the strip and the front of the plates in the neighbourhood of the strip. The distances between the plane from which the ions are emitted and the slit-planes will, therefore, be less than this by the thickness of the platinum plus the thickness of the layer of salt. The former was .002 cm. and the latter about as much. The platinum strip was arranged so that it curved away from the plates when heated. It is believed that the increase of the distance due to the curvature more than counterbalances the effect of the neglected thickness. The effect of these errors in the distance is probably to make the values of m deduced from the observations too low. On the other hand, there is an intrinsic error, due to the apparatus not satisfying the theoretical conditions, which tends to make m too high. It is believed that these effects just about balance one another when the value of z as determined above is substituted in the formula. At any rate, it is clear that however considerations of this kind may affect the absolute values of e/m and m , they can have very little influence on the relative values of these quantities.

Preliminary Experiments.

On account of the very close similarity in the properties of the alkali metals and their compounds, we should expect that the sulphates of the different alkali metals would give rise to positive ions whose values of e/m and m would be determined by the atomic weight of the metal under investigation. This conclusion is to be expected whether the ions contain more than one chemical atom or not; for it is to be expected, from the similarity of the properties of the alkali metals already alluded to, that the ions from the different metals will be similarly constituted whatever their constitution may be. For example, if the ions from lithium sulphate were molecules of Li_2SO_4 which had lost a negative electron, we should expect the ions from potassium sulphate to be molecules of K_2SO_4 less a negative electron: if the ions from lithium sulphate were atoms of lithium less a negative electron, we should expect the ions from potassium sulphate to be atoms of potassium less a negative electron, and so on. We should thus expect the values of e/m to exhibit a regular diminution, and those of m a regular increase in proceeding from lithium sulphate to caesium sulphate. The difference of the values in these sequences will, of course, be greatest if the ions are the atoms of the elements whose compounds are used: if the ions are themselves of a compound nature, the differences will be not be so great, but will be in the same direction. Thus both the absolute values of e/m and m and their relative values, also, should afford us valuable information as to the structure of these ions.

The first experiments made were of a rather qualitative character. The method was adopted of comparing the deflexion of the ions of the salt used with that of the platinum ions from the same strip and in the same magnetic field. It was found that the ions from sodium sulphate were deflected rather more, and those from potassium sulphate rather less, than those from platinum. This was in accordance with previous expectation. A surprise was in store, however, when lithium sulphate was tried. It was found that on the first trial the ions from this substance were deflected to almost exactly the same extent as those from platinum but rather less if anything, whereas on the view expressed above the deflexion for the ions from lithium sulphate should have been very much bigger than for those from the two metals of higher atomic weights. Instead of this, the values for lithium sulphate were between those for the sulphates of sodium and potassium.

It occurred to the author that the explanation of this result might be as follows: It is well known that at low temperatures, when the salts of the alkali metals are ionized by heat, the amount of ionization produced is much greater the higher the atomic weight of the metal used. This tendency is well shown, for example, in experiments by Smithells, Dawson, and Wilson* on the conductivity imparted to flames by alkali salt vapours. Now lithium sulphate is certain to contain the sulphates of potassium and sodium as impurities, and these will give rise to an amount of ionization more than proportionate to the amount of them which is present. In fact, it is quite conceivable that the bulk of the ionization from the lithium sulphate at first may be caused by the comparatively small quantities of the sulphates of the metals of higher atomic weight mixed with it. On this view, we should expect that the value of e/m would increase and that of m diminish with continued heating of the lithium sulphate, and for two reasons. In the first place, the decomposition and consequent removal by ionization is greater the greater the atomic weight, and, in addition, the volatility of the salts of the alkali metals increases as the atomic weight of the metal increases. Careful observations were therefore made from time to time on the deflexion, in a magnetic field, of the positive ions from a specimen of lithium sulphate, which was heated continuously for about 70 hours. It was found that the deviation of the ions produced by the magnetic field gradually increased with the lapse of time, and in fact the results were in complete accordance with the view that the initial values were due to the presence of salts of the metals of higher atomic weight.

The results of the observations on the different salts will now be considered in detail in the order of the atomic weights of the constituent metals, commencing with lithium sulphate.

LITHIUM SULPHATE.

The lithium sulphate used was supplied as pure by Messrs. Eimer & Amend, New York. As was the case with all the sulphates investigated, experiments were first made with the initial ionization from the platinum itself. The residue of this was then driven off by heating all night at a somewhat higher temperature. After the emission of positive ions from the platinum itself had fallen to a small value, the platinum was taken down and a small quantity of lithium sulphate laid

* Phil. Trans. A. vol. 193. p. 105 (1899).

on the strip. The latter was then heated until the salt melted. In this way, a uniform layer of the salt was obtained over the whole of the front surface of the strip. The apparatus was again set up and exhausted. The distribution of the positive ionization on the opposite planes was now determined after the salt had been heated for different lengths of time. Throughout this investigation a difference of potential of 200 volts was maintained between the plane containing the strip and that containing the slit, the strip being positive. In all the experiments with lithium sulphate the transverse magnetic field was of strength 4700 lines per cm., and measurements were made with it first in one direction and then in the other. In some cases experiments were also made in the absence of a magnetic field. The distance z between the plates near the slit and the back of the strip was measured, by focussing with a microscope furnished with a micrometer arrangement for vertical displacements, from time to time during the course of the experiments. The apparatus was continuously exhausted by means of a Gaede pump, and the pressure recorded on the McLeod gauge was kept below $\cdot 001$ mm. In some of the experiments it was as low as 10^{-5} mm. Provided the pressure is less than $\cdot 01$ mm., its actual value does not seem to influence the results.

The results of the experiments can best be exhibited by means of curves showing the fraction of the total number of ions received by the plates which pass through the slit for different positions of the latter. The rationale of this is fully explained in the first of the papers already referred to*. The units used are arbitrary since a capacity of $\cdot 001$ microfarad was always placed in parallel with the plates, whereas there was no capacity except that of the electrometer and its connexions attached to the slit electrode; and the capacity of the electrometer and its connexions was not determined. It was, however, the same in all the experiments.

The results of the experiments on the ionization from platinum alone are shown in fig. 1 (Pl. XX.). These represent two successive series of measurements with the magnetic field in each direction. The points for the first series are shown thus: $\oplus$, and for the second series thus: $\times$. Although the curves are not quite coincident, the displacement of the maximum which gives the values of e/m and m is practically identical for both sets. At the beginning of this experiment, two measurements of the value of z gave $\cdot 480$ and $\cdot 478$ cm.

* Phil. Mag. [6] vol. xvi. p. 740 (1908).

respectively, and at the end $\cdot 489$ and $\cdot 485$. The mean of these values of z is $\cdot 483$ cm.

The observations taken immediately after the lithium sulphate was placed on the strip are exhibited in fig. 2. Here again we have the result of two determinations taken immediately after one another, for each direction of the magnetic field, the first being shown thus: $\oplus$, the second thus: $\times$. As before, the corresponding curves are not quite identical but the displacement of the maximum is the same for each pair. It is slightly less than that for platinum, indicating that the ions emitted by fresh lithium sulphate are slightly heavier than those emitted by that metal. The curves are also rather broader than those for platinum. Immediately before this series of measurements was made the value of z was measured and found to be $\cdot 485$ cm. These curves have only one maximum, showing either that the ions are all of one kind, or at any rate that the value of e/m for the different kinds, if more than one, does not vary enough for them to be separated by the magnetic field used.

The next curve (fig. 3) shows the effect of heating the lithium sulphate continuously for twelve hours. The right and left hand curves, points thus: $\oplus$, are those obtained when the magnetic field is applied; the central curve, points thus: $\times$, is what is obtained in the absence of the magnetic field. We see that the curves obtained in the presence of the magnetic field are now more complex than before. Instead of having a single maximum we now have two maxima separated by a minimum. The obvious explanation of this is that there are now two kinds of ions present which are differently deflected by the magnetic field. That this is the correct explanation is shown by the curve obtained in the absence of the magnetic field. This possesses only one maximum, and is in all respects similar to those obtained earlier, in the magnetic field. The shape of this curve entirely precludes the possibility that the humps are due to some irregularity which has developed in the distribution of the salt along the strip.

The distance between the two inner humps, corresponding to the heavier particles, is about the same as that given by a new platinum wire or a fresh specimen of lithium sulphate; whereas the distance between the two outer humps is very much greater and corresponds to ions of much smaller mass. The value of z in this experiment was $\cdot 477$ cm.

As the heating is continued it is found that the outer hump grows whilst the inner hump diminishes. After 30 hours heating the outer humps were much bigger than the inner

ones. The whole pattern was also rather irregular, and part of this irregularity persisted in the absence of the magnetic field. This distortion is probably due to the salt not being so uniformly distributed after all this heating as it was at first. The appearance presented after 44 hours heating is shown in the next curve (fig. 4). Here the main part of the curve consists of the two well-marked outer humps. The value of z was not measured at this stage, but it may be taken as 480 cm., which is half way between the value 477 cm. after 12 hours heating and the value 4835 cm. attained after 70 hours heating.

When the heating was continued further, it was found that the ionization got smaller and smaller, so that increasing temperatures had to be employed in making the measurements. In addition, a small hump gradually developed on the inside of the outer one. This got larger whilst the old one became smaller and smaller. After about 70 hours heating there was again practically only one hump, and the displacement of this on reversing the magnetic field was very little bigger than that given by the ions emitted from fresh platinum. The curves obtained after heating for 70 hours are shown in the next diagram (fig. 5). The breadth and irregularity of the curves is probably due to there still being a small amount of the lithium salt present. Two measurements of z at the end of this experiment gave 484 and 483 cm. respectively, the mean of which is 4835 cm. On attempting to carry the experiment still further it was found necessary, in order to get a measurable amount of ionization, to raise the strip to a temperature so high that it melted.

The foregoing results can be readily explained if we assume that the positive ionization emitted by fresh lithium sulphate is due to the salts of the alkali metals of higher atomic weight (sodium and potassium) which it contains as impurities; that the ionization which these substances produce at a low temperature is so great in comparison that it completely masks that due to the much larger quantity of lithium sulphate present, and that the continued heating drives off the sulphates of higher atomic weight, so that we then get the much bigger displacements due to the lighter ions given off by the lithium salt itself. Finally if the heating is continued long enough the lithium salt is driven off. We then get, at a much higher temperature, a small quantity of the ionization characteristic of the platinum itself.

The evidence in favour of this view has so far been of a rather qualitative nature. It receives additional support when the values of e/m and m deduced from the above

experiments are considered. The numerical results are exhibited together in the following table:—

Lithium Sulphate—Positive Ions.

Substance.	Time heated (hours).	z (cms.)	V (volts).	H (lines per cm. ²)	x ($1=0.63$ cm.).	e/m (E.M. units).	m ($H=1$).
Pt	0	483	200	4700	.99	297	32.5
Li ₂ SO ₄ ...	0	485	200	4700	.95	269	35.9
" ...	12	477	200	4700	.85	231	41.8 *
" ...	12	477	200	4700	2.35	1760	5.5 †
" ..	44	479	200	4700	2.35	1735	5.57
" ...	52	481	200	4700	2.05	1300	7.43
" ...	70	4835	200	4700	1.25	470	20.6

* The value calculated from the two inside humps.

† The value calculated from the two outside humps.

The first column gives the material experimented with, the second shows the time the lithium sulphate had been heated, the third gives the distance in cms. between the back of the strip and the plate, the sixth gives half the displacement of the maximum produced by reversing the magnetic field given in the fifth column, whilst the meaning of the numbers in the remaining columns are obvious. The values of m represent the ratio of the mass of the ions to that of an atom of hydrogen on the assumption that the ions carry the same charge as that carried by an atom of hydrogen in electrolysis. The value of e/m for hydrogen was taken to be 9.66×10^3 E.M. units.

The value of m for the platinum ions (32.5) is not very different from the mean (25.7) of the values given by Richardson and Hulbirt*, and is within the limits of the range of values found by them. On the view that the positive ions emitted by hot metals are due to the presence of alkaline impurities, this value would correspond to that from a mixture of potassium (atomic weight 39.15) and sodium (atomic weight 23.05). This is on the assumption that the ions are positively charged atoms of the metals in question. We shall see that this is substantiated in so far that the positive ions emitted by the sulphates of the alkali metals are atoms of the metals they contain.

The value of m for the ions from fresh lithium sulphate (35.9) is very near the atomic weight of potassium, and is in

* *Loc. cit.*

agreement with the view that the initial ionization is due principally to the admixture of salts of this element, perhaps with some sodium in addition. The value 41.8, for the inner of the humps which developed after the twelve hours heating, again is of approximately the same magnitude, pointing to the presence in smaller relative amount of the same impurity. The value (5.5), calculated from the two outer humps, agrees satisfactorily with the atomic weight of lithium (7.05). A still better agreement is obtained after the inner humps have disappeared, and we obtain the value of m which presumably corresponds to the pure lithium salt. The value after 44 hours heating was found to be 5.57, and after 52 hours heating 7.43. The mean of these values is 6.5 instead of 7.05. The value (20.6) obtained after 70 hours heating is what we should expect if it were due to the platinum ions, for which m was found to be 32.5, mixed with a certain amount of the more deviable ions from the lithium salt. Thus the view we have taken of these effects gives a satisfactory account of the phenomena exhibited by lithium sulphate. The position is still further strengthened when the salts of the other alkali metals are examined.

SODIUM SULPHATE.

The specimens of sodium and potassium sulphates used were presented to the author several years ago by Professor H. A. Wilson. They had been specially prepared for use in obtaining standard temperatures from their melting-point, and are believed to be very pure. At any rate, the sodium sulphate is not likely to contain anything with more capacity for emitting ions than itself, with the possible exception of traces of potassium sulphate. We should therefore expect that sodium sulphate would behave quite differently from lithium sulphate. The deflexion of the maximum by the magnetic field ought to be quite constant, except in so far as any trace of potassium sulphate present might make the deflexion a little smaller at first than later. There ought to be no development of widely divergent humps as in the case of the lithium sulphate. As a matter of fact this is exactly what was observed.

As before, two sets of curves for the initial ionization from the platinum strip (a fresh one) were taken. The distance between the maxima for one set of curves was 1.96 turns of the screw and for the other 2.04 turns, the mean being 2.00 turns. The value of z was .492 cm. The strength H of the magnetic field in this set of experiments was 4650 lines per cm. The above numbers give $m = 33.7$, which

is practically identical with the value found from the specimen of platinum used in the experiments on lithium sulphate.

In this set of experiments it was not possible to make measurements on the ionization from sodium sulphate until the heating had gone on for about two hours. Three sets of observations were taken, after heating for two hours, eight hours, and twenty-four hours respectively. The results are shown in fig. 6. In this experiment the field strengths &c. had the following values:— $V=200$ volts, $H=4650$ lines per cm.², $z=.497$ cm.

It will be seen that the maxima are deflected to nearly the same extent in every case. However the first curves, points thus: $\times$, obtained after two hours heating, give a slightly smaller deviation (2.3 turns) than the others and lead to the value $m=26.6$. The next, points thus: $\times$, after eight hours heating, give a deviation of 2.45, corresponding to $m=23.4$. After heating twenty-four hours, points thus: $\oplus$ and $\boxtimes$, the deviation is practically unaltered at 2.5 turns, corresponding to $m=22.5$. The effect of continued heating on the sodium sulphate is clearly very different from that of lithium sulphate.

The very small size of the humps obtained after heating the sodium sulphate for twenty-four hours seemed suspicious, and was investigated further. It was found that these two humps represented only an isolated portion of the curve, which really extended over a much greater length in the direction of x than that shown in the figure. Detailed observations taken after thirty hours heating showed that a measurable fraction of the ionization passed through the slit all the way from $x=10$ turns to $x=11$ turns. There were several humps in the curve, which resembled a panoramic view of a range of mountains. There was, however, no evidence of any splitting up of the ions into groups characterized by different values of e/m . The patterns were displaced as a whole by the magnetic field, corresponding points being displaced about equal distances, and the form of the curve was the same in the absence of the magnetic field as with it. It was quite different from the behaviour of lithium sulphate shown in fig. 3. The peculiarities observed could be explained if the sodium sulphate after continued heating tended to collect in lumps at the edges of the strip where the electric field is irregular. When the apparatus was taken down, the salt which was left was too small in amount to be visible. It was observed, however, that the strip had become contorted somewhat, which would also explain the peculiar effect encountered.

Another set of observations made on sodium sulphate

confirms the preceding results and brings out one or two new points as well. This set is represented in fig. 7. The curves at the top (fig. 7, A), points thus: $\times$, exhibit the effect of heating the platinum by itself. In these experiments $V=200$ volts, $H=4700$ lines per cm.^2 , and $z=.556$ cm. The displacement 2.85 turns for the platinum ions leads to the values $e/m=349$ and $m=27.7$, in agreement with those found previously.

Three curves are given, fig. 7, B, representing observations on sodium sulphate. Those with points thus: $\oplus$, were obtained when the salt was first heated. It will be noticed that they are broader than and not so high as the later ones. The displacement of the maximum, 2.95 turns, corresponds to $m=25.9$. It is greater than that for the platinum ions, and less than that, 3.3 turns, obtained after the sodium sulphate had been heated longer. The two remaining curves were taken in succession after the salt had been heated for about fourteen hours. The curves with points thus: $\times$, were taken first, those with points $\oplus$ and $\boxed{\times}$ later. The displacement of the maximum is the same in both cases, and the character of the curves is very much the same. The value of m calculated from the displacements is 22.0.

The greater value of m and the greater breadth of the curves obtained on first heating is readily explained if we suppose that the sodium sulphate contains a small quantity of potassium sulphate which would be much more effectively ionized, at the lower temperature at which the observations commenced.

The results of the measurements with the sodium sulphate are gathered together for reference in the following table. The units &c. are the same as in the table for lithium sulphate.

Sodium Sulphate—Positive Ions.

Substance.	Time heated.	z (ions).	V (volts).	H (lines per cm.^2).	x (1.0635 cm.).	e/m (E.M. units).	m ($H=1$).
Platinum .	0	.492	200	4650	1.00	287	33.7
Na_2SO_4 ...	2	.497	200	4650	1.15	363	26.6
Na_2SO_4 ...	8	.497	200	4650	1.225	413	23.4
Na_2SO_4 ...	24	.497	200	4650	1.25	430	22.5
Platinum .	0	.556	200	4700	1.425	349	27.7
Na_2SO_4 ...	0	.556	200	4700	1.475	373	25.9
Na_2SO_4 ...	13	.556	200	4700	1.60	439	22.0
Na_2SO_4 ...	15	.556	200	4700	1.60	439	22.0

POTASSIUM SULPHATE.

Several sets of observations were made on the ionization from the fresh platinum strip which was used in this experiment. In these experiments the values of the field &c. were $V=200$ volts, $H=4650$ lines per cm.², and $z=.501$ cm. Immediately after the heating of the strip was commenced the displacement $2x$ of the maximum was found to be 2.42 turns, giving $e/m=390$ and $m=24.8$. After heating for about one hour $2x$ had become 2.28 turns, giving $e/m=346$ and $m=27.9$. After six hours heating it was found that $2x=2.00$ turns, $e/m=266$, and $m=36.3$.

The gradual increase of m as the heating is continued is in agreement with the author's previous experiments on platinum*. It would seem to indicate that the source of the positive ionization of lower atomic weight from platinum is more easily driven off by heating than that of higher atomic weight. The results are in agreement with the view that the ions of lower atomic weight are sodium atoms, but as the substance of higher atomic weight is less easily driven off by heat, it would appear that some impurity other than potassium or its salts has to be looked for. So far the writer has not been able to observe the development of humps in the curves for the ionization from platinum similar to those from lithium sulphate. This would seem to indicate, if the observed change in the nature of the ions is real, that it takes place very gradually, as there is no evidence of the simultaneous emission of two groups of ions with widely separated values of e/m . The experiments on the platinum ionization were not continued further, as the ionization at the temperature at which the experiments were being carried out became very small at the end of the last experiment.

The curves given by potassium sulphate itself were very simple in character. They consisted of just a single hump, and remained almost unchanged during sixty hours heating. At the same time the displacement of the maximum was constant within the limits of experimental error. After about eighteen hours heating of the salt, however, the curves broadened very considerably, but this may have been due to some temporary contortion of the strip as it disappeared later, and all the time afterwards the curves were simple as at first and gave the original value of e/m .

The results of the first few heatings of the salt are exhibited in fig. 8. The left-hand curve with points thus :— $\times$, was taken as soon as the heating commenced. The magnetic

* Cf. Phil. Mag. [6] vol. xvi. p. 759 (1908).

field was then reversed, and the curve with points thus :— $\times$, taken. The field was again changed back to its original value and the position of the first maximum redetermined. The points are shown thus :— $\overline{\times}$. The position of the first maximum was found to be unchanged within the limits of experimental error.

The curves with broken lines, points $\oplus$, represent similar observations taken after six hours heating. Although the positions are displaced a little, the displacement of the maximum due to the field is the same as in the preceding case. In the experiments represented in this diagram the values of the numerical quantities were :— $V=200$ volts, $H=4600$ lines per cm., $z=.501$ cm., and $2x=1.98$ turns. These values, which are the same for both sets of observations, give $e/m=261$ and $m=37.0$.

Similar sets of observations were taken after 18, 24, 36, 42, and 60 hours heating. As, except for the temporary broadening mentioned above, which was observed after eighteen hours heating, all the curves were similar in character, it will be sufficient to give the last one of them. This is shown in fig 9, and represents the results obtained after sixty hours heating. The data pertaining to this curve, as well as the other observations mentioned, are given in the following table :—

Potassium Sulphate—Positive Ions.

Substance.	Time heated (hours).	z (ions).	V (volts).	H (lines per cm.).	x (1.0635 cm.).	e/m (E.M. units).	m ($H=1$).
Platinum .	0	.501	200	4650	1.21	390	24.8
„	1	.501	200	4650	1.14	346	27.9
„	6	.501	200	4650	1.00	266	36.3
K ₂ SO ₄ ...	0	.501	200	4650	.99	261	37
„ ...	6	.501	200	4650	.99	261	37
„ ...	24	.486	200	4650	.93	261	37
„ ...	36	.486	200	4650	.95	272	35.5
„ ...	42	.486	200	4650	.94	266	36.3
„ ...	60	.486	200	4650	.94	266	36.3
Mean value of m for K ₂ SO ₄ = 36.5							

It will be seen that the different values of e/m and m for

the positive ions from potassium sulphate given by this set of observations are all very near one another and quite close to the value for the atom of potassium. The atomic weight of this metal is 39.15.

Another set of observations on potassium sulphate gave for the initial ionization from platinum $2x=1.88$ turns. The corresponding quantity immediately after heating potassium sulphate was found to be 1.80 turns. The value of z for this experiment was not measured, so that the values of e/m and m could not be calculated. The relative values for platinum and potassium sulphate, however, confirm those obtained in the more complete series of experiments just described.

RUBIDIUM SULPHATE.

The ionization obtained from the platinum strip used in this experiment gave a high value of m , probably owing to the strip having been heated for some time before the measurements were made. The data for this part of the experiment are:— $V=200$ volts, $H=4700$ lines per cm.², $z=.512$ cm., and $2x=2.00$ turns. These values give $e/m=240$ E.M. units and $m=40.3$.

The results of the observations on rubidium sulphate are exhibited in fig. 10 (Pl. XX.). These were taken shortly after commencing to heat the salt, but the exact interval of time was not recorded. The left-hand curve with points thus:— $\times$, was taken first. The magnetic field was then reversed, and the right-hand curve with points thus:— $\times$, obtained. The original direction of the magnetic field was now restored, and the left-hand points $\oplus$ were obtained. The field was again reversed, giving the right-hand points, $\oplus$. The displacement between the first two maxima is 1.24 turns, that between the two second 1.30 turns. The mean is 1.27 turns. The other data for this experiment are $V=3200$ volts, $H=4700$ lines per cm.², and $z=.506$ cm. These give $e/m=101$ and $m=96$. The atomic weight of rubidium = 85.5.

The experiments with rubidium sulphate were not continued further, as it was thought at the time that this was a satisfactory agreement. It may be, however, that the rubidium sulphate contains some caesium as an impurity, and that further heating would have increased the value of e/m . It is worthy of note in this connexion that rubidium is the only element so far for which the value of m is distinctly above the atomic weight, the other cases tending to fall

below it. However, the difference is not greater than the error of observation might well account for.

The specimen of rubidium sulphate used was purchased from Messrs. Eimer and Amend. It was not stated to be especially pure.

CÆSIUM SULPHATE.

Two sets of observations were made with the ionization from the fresh platinum strip used in this experiment, one immediately after the heating was started and the other a few hours later. The first led to the values $2x=2.05$ turns, $e/m=344$, $m=28.2$, and the second, $2x=1.95$ turns, $e/m=295$, $m=32.7$.

This increase with lapse of time in the value of m for the ions from platinum is in agreement with that already discussed under the heading of potassium sulphate.

The following data were the same for all the experiments in this series, whether with platinum alone or with cæsium sulphate:— $V=200$ volts, $H=4700$ lines per cm.², and $z=474$ cm.

The results of the observations on cæsium sulphate are all shown in fig. 11. The first two curves, points:— $\times$, were taken immediately after the heating had started. It will be noticed that these are distinctly broader than the later curves, and the displacement of the maximum was greater. The displacement in this case was $2x=1.125$ turns, giving $e/m=101.8$, $m=95$.

The curves with points $\oplus$ were obtained after eighteen hours heating. The displacement now is $2x=.85$ turns, giving $e/m=59.1$ and $m=163$. The remaining curves, points $\oplus$ and $\boxtimes$, represent the results after twenty-three hours heating. The displacement is again $2x=.85$ turns, giving the same values of e/m and m as the last.

It may be that the greater breadth of the curves and the greater displacement of the maxima obtained initially represents a real difference in the ionization. It is, however, difficult to be certain about the matter, as the displacements with these heavy ions are small, and the probable experimental error is correspondingly great. The mean of the three measurements gives $m=140$. The atomic weight of cæsium is given as 133.9

The specimen of cæsium sulphate used was prepared by the action of pure sulphuric acid on the chloride. The latter was bought from Messrs. Eimer and Amend, with no specification as to its purity.

General Considerations.

The values of e/m and m which, according to the view of these phenomena developed in the present paper, are characteristic of the positive ions emitted by the pure sulphate of the alkali metals, are collected together in the following table. The values which are believed to be due to the presence of impurities in the material are omitted from the table.

Substance.	Time heated (hours).	e/m (E.M. units).	m (H=1).	Average value of m .	Atomic weight of metal.
Li_2SO_4	12	1760	5.5	...	7.05
Li_2SO_4	44	1735	5.57	...	7.05
Li_2SO_4	52	1300	7.43	6.2	7.05
Na_2SO_4	8	413	23.4	...	23.05
Na_2SO_4	24	430	22.5	...	23.05
Na_2SO_4	13	439	22.0	...	23.05
Na_2SO_4	15	439	22.0	22.5	23.05
K_2SO_4	0	261	37.0	...	39.15
K_2SO_4	6	261	37.0	...	39.15
K_2SO_4	24	261	37.0	...	39.15
K_2SO_4	36	272	35.5	...	39.15
K_2SO_4	42	266	36.3	...	39.15
K_2SO_4	60	266	36.3	36.5	39.15
Rb_2SO_4	...	101	96	96	85.5
Cs_2SO_4	0	101.8	95	...	132.9
Cs_2SO_4	18	59.1	163	...	132.9
Cs_2SO_4	23	59.1	163	140	132.9

The numbers in the last three columns of the table show conclusively that *the positive ions emitted by the sulphates of the alkali metals are atoms of the constituent metal*. The range of e/m , m , and of the atomic weight for the different metals is so great that, although the accuracy of the measurements is not, perhaps, all that might be desired, particularly in the case of the elements of higher atomic weight, nevertheless the general agreement of m over so wide a range is such as to leave no room for escape from the above conclusion.

It also follows that *the positive ions emitted by the sulphates*

of the alkali metals carry the same charge as that carried by an atom of hydrogen in electrolysis, since this assumption has been made in calculating the values of m and leads to consistent results. We therefore conclude that the positive ions emitted by these substances when heated have the same structure as that which is generally attributed to the nuclei of the positive ions to which the same substances give rise in solution. In other words, *they consist of one atom of the basic metal which has lost a negative electron.*

The similarity between the thermions and the electrolytic ions appears to end with the positive ions. So far the only negative thermions which have been detected have a very large value of e/m and are negative electrons. There is no evidence of the existence of negative thermions similar in structure to those which occur in solution.

The present investigation does not throw any definite light on the chemistry of the processes involved. Since the positive ions are atoms of the metal, it is clear that they must get free from the rest of the molecule somehow. It is possible that the first decomposition consists of a splitting up of the sulphate into positively charged atoms of the metal and a negatively charged SO_4 group, as is the case in solution. This would then presumably be followed by the breaking up of the negatively charged group into its chemical constituents together with a negative electron. The results of the experiments neither affirm nor deny this view. It seems possible that valuable evidence in this connexion might be obtained by looking for a relation between the amount of positive and of negative ionization produced by heated salts. Experiments with this end in view are being instituted. In any event, the present investigation shows that the expulsion of a positively charged atom of the metal is a salient feature of the ionization of heated salts.

The balance of evidence at present is not in favour of the view that the positive ions produced by salt vapours in flames at a high temperature are identical with those here investigated. Their velocities have been measured by different experimenters, and there is a general agreement that the positive ions produced by the salts of all the alkali metals have the same velocity under unit field. This result would not be expected if the ions were atoms of the metals. The absolute values of this common velocity given by different observers are rather divergent. For instance, H. A. Wilson finds 62 cm. per sec., Marx finds 200 cm. per sec., and Moreau 80 cm. per sec. Nevertheless, all these values are higher than what would be expected if the ions were atoms of the

metal, particularly in the case of the elements of higher atomic weight. They are, however, in very good agreement with the value calculated from the formula $u = \frac{1}{2} \frac{e \lambda}{m v}$, where u is the velocity under unit field, e the charge, m the mass, λ the mean free path, and v the mean velocity of agitation of the ions, on the hypothesis that they have the same structure as those discovered by Sir J. J. Thomson * in the canal rays. Moreover, the ratio of the velocity of the negative to that of the positive ions in flames at high temperatures is in good agreement with this view.

Outside of solutions the number of cases of positive ions of which the structure has been definitely determined is not very large. The only ones which occur to the author are the α particle, which Rutherford showed to be an atom of helium carrying twice the electronic charge, and the canal rays in different gases, for which the mass of the carriers has been investigated by Wien, Stark, and Thomson. With the exception, possibly, of the particles having a high value of e/m , isolated by Thomson from the canal rays, all these researches agree with the results of the present investigation in making the primitive positive ion an atom of some known chemical element which has lost one or more negative electrons.

In concluding I wish to thank Mr. Irving B. Crandall, A.B., graduate student in physics, and my assistant, Mr. Cornelis Bol, for their help in taking the observations.

Palmer Physical Laboratory,
Princeton, N. J.

CXI. *The Positive Thermions emitted by the Salts of the Alkali Metals.* By O. W. RICHARDSON, M.A., D.Sc.,
Professor of Physics, Princeton University†.

IN the preceding paper the author has shown that the positive ions emitted by the sulphates of the different alkali metals are atoms of the constituent metal carrying a single electronic charge. The sulphates were used in the investigation because they are readily obtainable in a state of reasonable purity and are comparatively non-volatile. There is no reason to expect that the sulphates are exceptional in regard to the positive ions they emit. We should, therefore,

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† Communicated by the Author.