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The Emission of Electrons under the Influence of Chemical Action

O. W. Richardson

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PHILOSOPHICAL TRANSACTIONS.

I. *The Emission of Electrons under the Influence of Chemical Action.*

By O. W. RICHARDSON, *F.R.S., Wheatstone Professor of Physics, University of London, King's College.*

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§ 1.—SEVERAL investigators have claimed that electrons are emitted from metals under the influence of chemical action, but the only claim* which seems well substantiated is that of HABER and JUST,† who found that when drops of cæsium or of the liquid alloy of sodium and potassium are attacked, at a low pressure, by a number of chemically active gases, the drops lose a negative but not a positive electric charge. The electric currents set up with the drops negatively charged are stopped by the application in a suitable manner of relatively small magnetic fields. This shows that the currents are carried by electrons emitted from the drops.‡

The object of the present investigation has been to obtain quantitative information about this interesting phenomenon, and, more especially, to ascertain the magnitude of the kinetic energy of the emitted electrons and the mode of its distribution among them. The importance of the subject lies in the fact that it is the only way, so far as I am aware, in which any information at all can be made available as to the distribution of energy among the individual products—molecular, atomic, ionic or electronic—of a chemical reaction. The majority of the experiments have been directed towards obtaining the curves showing the relation between the chemical electron current and the applied electromotive force for the case of a small spherical source concentric with a large spherical electrode. If the currents are small and the gas pressure is low, so that the motion of the liberated electrons is determined entirely by the applied electric field and is interfered with neither by the molecules of the gas nor by the fields of force arising from other electrons, we should anticipate that these electron currents would exhibit saturation with zero applied potential difference; subject to the additional proviso

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* Possibly some of the cases examined by REBOUL ('C. R.,' vol. CXLIX., p. 110 (1909), and vol. CLII., p. 1660 (1911)), may turn out to be an exception to this statement.

† 'Ann. der Physik,' vol. 30, p. 411 (1909); *ibid.*, vol. 36, p. 308 (1911).

‡ A survey of the previous work in this and allied fields, together with an account of the results of some of the earlier experiments of the present research, will be found on pp. 290–298 of my book 'The Emission of Electricity from Hot Bodies' (London, 1916). It will be seen that the earlier experiments gave results which differ in some important particulars from those obtained later under more satisfactory conditions. *Cf.* also *ibid.*, pp. 49 *et seq.*, and pp. 128 *et seq.*

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that the electrons are liberated by the chemical action in such a manner that for practical purposes they can be considered to be clear of the fields of force of the atoms or molecules of origin. As to the validity or otherwise of this last assumption there was no prior evidence, but the experiments show that it is at least approximately satisfied and that small accelerating electric fields have little or no effect in increasing the electron emission. Subject to the validity of the assumptions referred to, the currents in any accelerating field should be constant, whilst their values in any retarding field will be a measure of the number of electrons whose kinetic energy when emitted exceeds the equivalent applied retarding potential difference. It should, in fact, be equal to the number of such electrons divided by the electronic charge. A characteristic curve satisfying such conditions for the case of the concentric spherical electrodes will therefore solve the problem so far as the total kinetic energy is concerned. Stated in this way the matter appears very simple, but it has been found in practice to be fraught with very serious difficulties which have taken a long time to overcome.

In all the experiments the metal acted on was a liquid alloy of sodium and potassium. In the majority of them this had an initial composition corresponding to the formula NaK_2. The alloy of this formula appears[*] to have the lowest melting point, and it is a quite mobile liquid at room temperatures. In some of the early experiments an alloy of higher melting point having the initial composition NaK was used. This fact will be mentioned when it is necessary to refer to those experiments. Where no specific reference to the composition of the alloy is made, it can be assumed that it was close to that given by the formula NaK_2. There is reason to believe that as the alloy is used the potassium is consumed faster than the sodium, with a consequent increase in the viscosity of the alloy. This effect is not so noticeable with the alloy NaK_2 as with NaK, which after a time becomes almost solid.

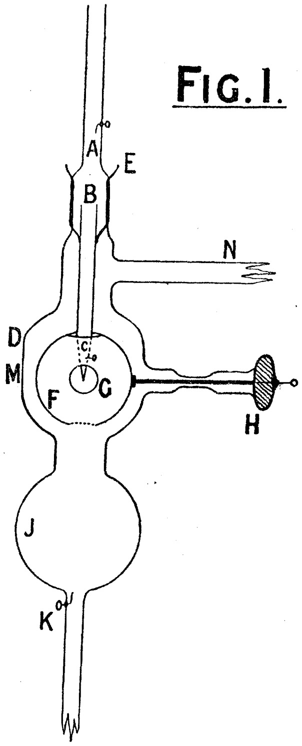
FIG. 1.

After a certain amount of preliminary skirmishing with apparatus of different designs, that finally used in the measurement of the characteristic curves for concentric spheres is shown in a working drawing in fig. 1. The supply of the liquid alloy was kept in a glass reservoir (a separating funnel) vertically above the tube A to which it was sealed. Between A and the reservoir was a glass stop-cock for regulating the flow of the alloy. A fine platinum wire trailed down the extension BC and was sealed through the glass between A and the stop-cock, and so brought to the outside of the apparatus for the purpose of applying any desired potential to the alloy in the tube BC. The dilated portion B of the tube AC was ground to fit air-tight into the neck of the main bulb D, and the joint could be sealed with mercury or wax at the

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[*] H. Le Chatelier, ‘Recueil de Constantes Physiques,’ p. 352, fig. 3 (Paris, 1913).

lip E. Below C the glass tube was drawn out to a fine nozzle, and the lower end of the tube about C was silvered, and the silver coating connected through to the alloy inside by a platinum wire sealed through the glass. The object of this was to maintain the outside of the tube at a definite electrical potential and to prevent trouble due to charges developing on the glass surface. Matters were so arranged that the nozzle was about a millimetre above the centre of the copper sphere F. This was attached to a stout wire supported by glass and connected through to the outside by the platinum seal shown at H. Part of the weight of the sphere was taken by a copper pin which butted into a small hump blown in the tube wall at M. The copper sphere, which was 5 cm. in diameter, was provided with openings in front and behind as indicated at G for the purpose of throwing a powerful beam of light of suitable frequency on to the drops which formed at the nozzle. The light was supplied by a Westinghouse Cooper-Hewitt quartz mercury vapour lamp and admitted through a tube sealed into the main bulb. This tube is at right angles to the plane of the figure, which does not show it. The end was ground flat and closed with a thin quartz plate cemented on with sealing-wax. The copper electrode F was provided with holes at the top and at the bottom. The drops fell through the lower hole into the bulb J, which was closed by a stop-cock below K. The alloy in J was connected to earth by the sealed platinum wire K. When a sufficient amount of the alloy had collected in J, dry carbon dioxide or nitrogen could be admitted at N, and the alloy forced back into the reservoir by a system of tubes and stop-cocks not shown. In this way a sample of the alloy could be used a considerable number of times without dismembering the apparatus.

The side tube N led to the phosphorus pentoxide bulb, the MacLeod gauge, the generator of inert gas just referred to, the pumping system (Gaede mercury pump and Geryk backing pump), and the generator of the chemically active gases under consideration. This consisted of a closed vertical tube about 5 mm. in diameter provided with a stop-cock and connected with a point near N through about a metre of similar glass tubing running horizontally. The gases dealt with were carbonyl chloride ($COCl_2$), chlorine (Cl_2), hydrochloric acid (HCl) and water vapour (H_2O). The three first were condensed into the generating tube by means of liquid air in a thermos vessel placed outside it, and the amount released into the apparatus could be varied by manipulating the height of the liquid air outside the generating tube. The water vapour was supplied from mixtures of water and sulphuric acid or from crystals of $CaCl_2\,6H_2O$.

Most of the experiments deal with $COCl_2$. Except in the most recent experiments this was prepared by boiling a mixture of 20 parts chloroform, 50 parts potassium bichromate and 400 parts sulphuric acid in a flask with a reflex condenser attached. The gas was freed from hydrochloric acid by bubbling through water, from water by bubbling through sulphuric acid, and from chlorine by passing through a U-tube containing small pieces of antimony, and then condensed in a freezing mixture of ice and salt. For the most recent experiments we have been able to secure a pre-war sample of $COCl_2$ by Kahlbaum. This seems to have the same properties as that which was prepared in the laboratory. The chlorine used was prepared by the action of hydrochloric acid on manganese dioxide, washed through sulphuric acid and condensed by liquid air. As a source of HCl gas strong hydrochloric acid was taken and the pressure reduced by cooling it to a low temperature. For H_2O, either water was taken and the vapour pressure reduced by mixing it with an excess of sulphuric acid, or crystals of $CaCl_2$ $6H_2O$ cooled below the room temperature were used.

The electrical arrangements were for the most part of an ordinary character and do not call for detailed description. The currents were measured by a quadrant electrometer having, except when otherwise stated, a sensitiveness of 570 divisions per volt. It is necessary that this instrument should be sensitive, as, although the currents dealt with are of considerable magnitude, the differences of potential to be investigated are small. One quadrant was connected to the point H in fig. 1, and the other to earth. In most of the experiments capacities varying from 0·01 to 1 mfd. were added to the earthed quadrant to reduce the deflections to convenient proportions. Potentials varying continuously by any desired amount between ± 20 volts could be applied to the drop, by means of a sliding contact on a rheostat fed by a battery with one end earthed, and were read by a double-scale Weston Voltmeter.

In some of the preliminary experiments the alloy was forced through the nozzle in a fine stream by admitting inert gas to a pressure of several atmospheres to the space above the main body of the alloy in the reservoir. This method was found to be unsatisfactory, as the stream was apt to get diverted on to the copper ball, owing to some minute particle of solid getting into the nozzle or to some slight deposit forming unsymmetrically at its edge. In the experiments for which data are given the driving pressure was only the atmospheric pressure, and the alloy flowed in a steady succession of uniform spherical drops. These were about 2 mm. in diameter and flowed at the rate of about 6 drops a minute in the experiments on which reliance is placed. Different nozzles have been tried and other conditions varied, so that experiments have been made with drops from about 1 mm. to 1 cm. in diameter and flowing at rates between about 1 per minute and 15 per minute. So far as I have been able to ascertain, the effects recorded are not influenced appreciably by the size and rate of the drops. The size (about 3 mm. diameter) and the rate (about 6 per minute) chiefly aimed at were chosen as being convenient to work with and easy to attain. It should be mentioned that with very slow drops irregular results may be obtained, as the emission is greatest when each drop starts, and falls off as the surface becomes protected by a layer of the reaction products. This effect is always present, but it does not appear to lead to serious trouble if the number of drops is not under four per minute.

With the viscous alloys containing a high percentage of sodium, exceptionally large and slow drops can be obtained. Some of these formed so slowly that they became covered with a visible white coating of the reaction products. As the drop increased in size this coating would fracture from time to time, exposing the bright alloy underneath the crack. Simultaneous with each fracture a sudden increase of the rate of electrometer deflection could be observed, owing to the increased emission from the clean alloy. Needless to say, no quantitative data are obtainable from experiments under such conditions. In the experiments on which reliance is placed, the rate of the drops was so rapid and the pressure of the attacking gas so low that no visible change occurred in the appearance of the surface of the drops.

In general it has not been found possible so to regulate the pressure of the attacking gas that the saturation current would stay constant. There is, however, no great difficulty in maintaining conditions so that the saturation current increases or diminishes in a regular manner with lapse of time. For example, a common method of procedure in dealing with $COCl_2$ has been the following :—Initially the $COCl_2$ would be strongly cooled by immersion of the generating tube in liquid air. The cock between the generator and the testing apparatus would then be opened and all the gas pumped out of the whole apparatus to a pressure of 0·001 mm. or less. The connection to the pumps would then be shut off and this vacuum would be maintained, provided the $COCl_2$ was well immersed in the liquid air. The alloy would then be allowed to drop, charged to a suitable negative potential, and the copper ball connected with the electrometer. If the electrical conditions were satisfactory there would be no deflection under these circumstances. The next step would be gradually to reduce the depth of immersion of the $COCl_2$ in the liquid air. This could be done by turning a screw table which supported the thermos bottle below the generator. Meanwhile continuous observation was kept on the electrometer spot, and at a certain stage a small movement would set in, showing that some active gas was beginning to reach the apparatus. It was generally convenient to raise the thermos bottle a little at this stage, as owing to a lag in the thermal changes the lowering process was generally somewhat overdone before the effects were perceptible. At about this stage transient effects would frequently be observed. These may be attributable either to a more volatile active contaminant present in the chemical used, or to some small trace of the latter which had condensed on the upper walls of the generator. These walls would no doubt warm up quickly when the liquid air was reduced. These transient effects would disappear after a little while, and the electron currents under a given applied voltage would be found to increase very steadily and deliberately as the generating tube gradually warmed up. If the rate of increase became inconveniently large, it could be checked by raising the liquid air and repeating the processes substantially as described until a complete set of observations had been obtained.

In some cases it was found preferable to work in a reverse manner, by allowing an excess of the active gas to flow into the apparatus and to observe the phenomena under examination as this gas was consumed. The consumption takes place rather slowly, probably owing to adsorption of the gas by the walls of the apparatus. A typical example of the diminution of the saturation current with time after admitting $COCl_2$, at a low pressure, is shown in fig. 2. The three curves correspond to units of current diminishing approximately by successive factors of 10, according to the different capacities, given on the respective curves, added to the electrometer system.

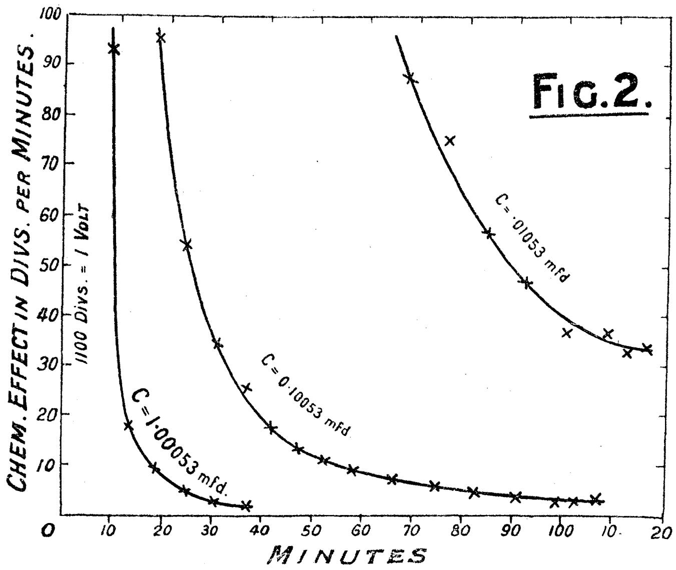

FIG. 2.

At the beginning of this experiment the pressure was less than 0·001 mm. and the admission of the $COCl_2$ did not show any ascertainable increase. It was therefore at most 0·001 mm. After 20 minutes the pressure had risen to 0·0015 mm., after 70 minutes it was 0·003 mm., and after 100 minutes 0·004 mm. These data strongly suggested that the admitted $COCl_2$ was mainly adsorbed and did not make itself felt on the gauge until the chlorine had been fixed and the carbon monoxide, a much less adsorbent gas, liberated. It will be seen that the chemical emission is most vigorous at first and rapidly falls off. The rate of decay, whether considered absolutely or in proportion to the amount of emission, steadily diminishes with lapse of time. This probably means that the active gas initially is that in the immediate neighbourhood of the drops, whereas later on it diffuses from more remote parts of the apparatus. It is probable that the rate of emission is proportional to the chemical action occurring, and that this is likewise proportional to the partial pressure of the active gas at the surface of the drop.

Whilst fig. 2 exhibits the decay of the effect in a typical way under the conditions referred to, it is not typical of the conditions holding during the majority of the measurements, when a much higher degree of constancy of the saturation current was attained. For example, in one set the saturation current only varied between the limits 26·5 and 31·5 during the whole experiment, which lasted over two hours. However, this change with time was always present and its effect had to be eliminated. To accomplish this, determinations of the current under varied conditions, as, for example, under different voltages, were alternated with measurements of the saturation current under some standard voltage. The results were then expressed as fractions of the standard saturation current ruling at the time the particular measurements were taken. The instantaneous value of the standard current was ascertained in various ways, depending on the rapidity with which it was varying. When the variation was small it was sufficient to take the arithmetic mean of the determinations of the standard current immediately preceding and following the measurement of the current under the given conditions. For somewhat larger degrees of variation the geometric means of the corresponding current values were found to give reliable results. Where the rate of variation was still more rapid, it was necessary to note the times of the various measurements, to plot a curve like fig. 2 showing the value of the standard current as a function of the time, and to ascertain from this curve the instantaneous value of the standard current at the time of the particular experiment. This method is, of course, one which is reliable under any circumstances; but, generally speaking, the rate of change of the standard current was so slow that it was not necessary to record the times at which the different measurements were made. This was an advantage, as each experiment involved a large number of settings and readings. The experimental manipulation was not particularly easy in any event, and each additional item which had to be recorded made a series of operations increasingly tiring and correspondingly liable to involve erroneous records.

This preliminary discussion will, I hope, give a general idea of the method of experimenting adopted. It will probably be more profitable to leave further details until the results of the particular experiments are dealt with.

§ 2.—*The Characteristic* (*Current — E.M.F.*) *Curve for Carbonyl Chloride.*

These data all refer to the system in which the source of emission is a spherical drop of the alloy NaK_2 of radius about 1 mm. surrounded by a concentric spherical electrode of copper of radius 2·5 cm. The pressure of the gas in the apparatus increased fairly uniformly with the duration of each experiment, the extremes of pressure recorded lying between the limits 0·001 mm. and 0·087 mm. With the exception of one experiment, the final pressure did not exceed 0·020 mm. It is probable that, in the exceptional case in which the final pressure of 0·087 mm. was recorded, there was a small leakage of air from outside the apparatus. The data afford no evidence that the maximum pressure of the $COCl_2$ ever exceeded 0·001 mm., and it may have been much less. The pressures recorded are those of the unabsorbed products of the reaction, and are therefore probably due to carbon monoxide. The sensitiveness of the electrometer was 570 divisions per volt, and the capacity of the electrometer and its connections 0·00012 mfd.

In most of the series of measurements a determination of the photo-electric current under the same voltage, due to the blue light from the mercury vapour lamp transmitted through a Wratten filter No. 50, was made immediately after each determination of the chemical current. The actual measurement made was that of the combined photo-electric and chemical emission, but the instantaneous value of the chemical current could be obtained from the determination immediately preceding after allowing for its variation with the time, and thus the value of the photo-electric current obtained by subtraction. The light transmitted by the filter is not strictly monochromatic, but for most practical purposes it can be regarded as consisting of the violet group lying between 4347 and 4358. Whilst I have not made a spectrographic examination of the light transmitted by this filter, it probably lets through a certain amount of the group 4046–4077 and a smaller amount of 4916. Consequently no particular quantitative reliance is placed on these photo-electric data, but they afford a valuable indication as to the difference between the chemical and photo-electric characteristic curves and also supply a useful guide as to the state of the surface of the alloy. Later on, when accurate photo-electric information became imperative, a monochromatic illuminator and a set of light filters were obtained. The reliability of these later photo-electric measurements, in so far as it is dependent on the monochromatism of the light used, is to be regarded as of a distinctly higher order than those dealt with in this part of the paper (see p. 23 *et seq.*).

Preliminary tests with this apparatus showed that the chemical-effect currents were not increasing appreciably when the negative (accelerating) potential on the drops was increased from 2 to 3 volts; so that — 3 volts was adopted as the potential for measuring the standard current. The procedure adopted, when photo-electric measurements were included, was first to measure the current with the light cut off at — 3 volts, then with the light still cut off at the voltage under test, say, x volts, then at x volts with the drop illuminated, then at — 3 volts again with the light off, then with the light off at a new voltage, say, y volts; then at y volts with the light on, then at — 3 volts with the light off again, and so on, until a complete set of data had been obtained. From these results the values of the relative chemical currents, *i.e.*, the values of the fraction obtained by dividing the current at the voltage under test by the instantaneous standard current and also the values of the photo-electric currents at the different voltages, were calculated in the manner already explained. When no photo-electric measurements were made the procedure was the same, except that the measurements with the drop illuminated were omitted. In all cases the successive settings and readings were made as rapidly as possible.

At first sight the results got in this way seemed very inconsistent. For example, in different experiments made at intervals perhaps of some weeks, but under conditions which were identical so far as I could ascertain, the relative currents at zero volts (as compared with — 3 volts as standard) would differ by 100 per cent. or more. Later on it appeared that the current at zero volts had vanished altogether, and that the current, instead of being approximately saturated, was increasing rapidly between — 2 and — 3 volts. However, when the precaution was taken of ensuring that the standard current was really on the saturation part of the curve, and when the results of the whole of the completed experiments were plotted and compared together, it was found that there was a definite method about these variations. This will be recognised from an inspection of fig. 3, which shows three of the characteristics as actually determined. The numbers alongside the crosses on curve 1 express the order in which

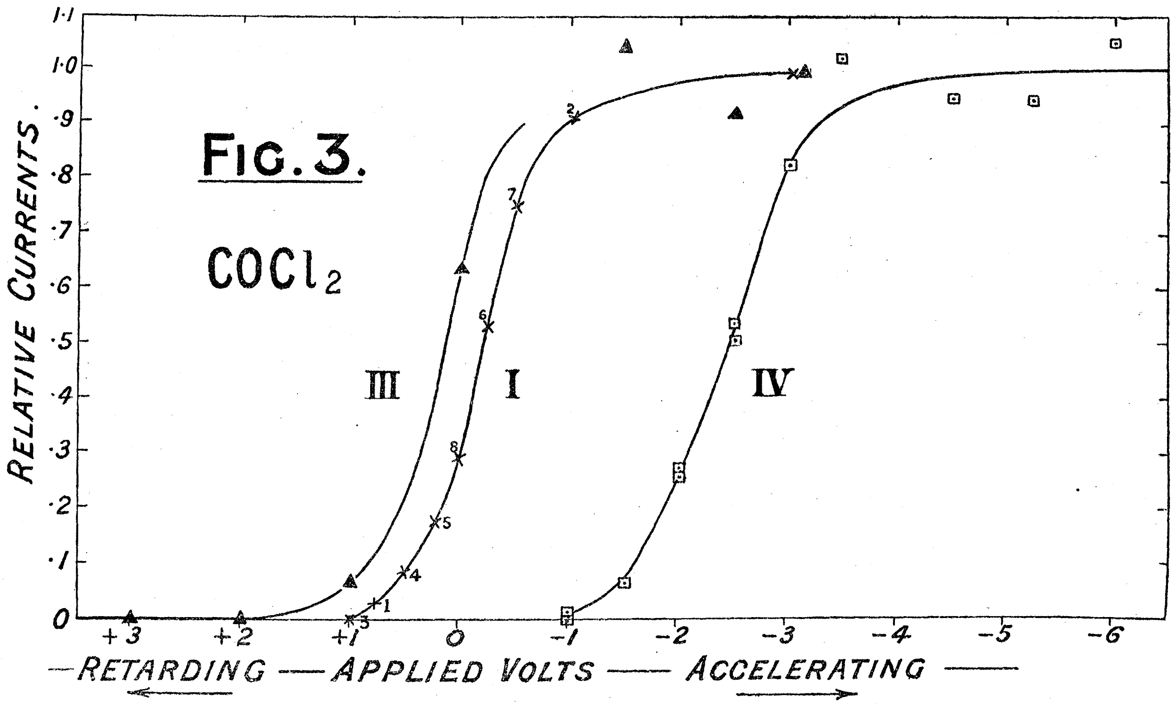

FIG. 3.

the different points were determined. It will be seen that each characteristic is consistent enough in itself. The variability, normally about 5 per cent., which seems rather pronounced on the flat part of the curves, is due to the cumulative effect of the errors inherent in the determination of the currents. The percentage error should be independent of the magnitude of the currents, and consequently is not so noticeable on the lower parts of the diagram where the relative currents are smaller. It is probable that the main source of error lies in the variation of the rate of emission with the growth of the drops, and it will be noticed that it is most pronounced in curve III., where the drops were formed with exceptional slowness (at the rate of 4 in 90 seconds). However, I believe that the accuracy of the measurements is sufficient to establish the conclusions which it is intended to draw from them.

It will be noticed that the shapes of the curves are all much the same, the most noticeable difference being that they are spaced widely apart on the voltage axis. In fact, it is clear from an inspection of fig. 3, that if any two of the curves are given suitable horizontal displacements, they can be made nearly to coincide with the remaining one. The explanation of such a result seemed obvious. The shapes of the characteristic curves are the same in the different experiments, but they occur at different places along the voltage axis. Now the voltage V plotted along this axis is that given by a voltmeter connected, in effect, across the gap between the drop of alloy and the copper sphere. The actual difference of potential across this gap is not equal to V, but is equal to V + K where K is the contact potential difference between the surfaces of the alloy and the copper sphere. If now the value of K is changing between one experiment and another, the observed results are completely accounted for. It will be necessary that K should exhibit an extreme variation of as much as 2·5 volts, but this does not seem a surprising requirement when it is remembered that the contact electromotive force between the alkali metals and copper is comparable with this amount. The changes in the contact electromotive force which occur are to be attributed to changes in the surfaces of the alloy and of the copper due to the gases and vapours to which they are exposed, and to changes in the copper surface due to splashing with the alloy and possibly to absorption of the vapours of the alkali metals by the copper.

To test this hypothesis, all the sets of observations with $COCl_2$ which were sufficiently complete to form a reliable guide were collected together and the relative currents in terms of the standard tabulated. In cases such as curve IV. in fig. 3, where the current was not saturated at — 3 volts, the standard voltage was chosen about 3 volts negative to a voltage at which the current was about 50 per cent. of the final saturation value. The precise value of this voltage does not matter much, as the current in this region is not varying with the voltage to an extent ascertainable by these experiments. What is important is that the standard current should be saturated, and it was convenient to employ the least voltage that would make sure of this. It was also felt that until more information was available about the phenomenon, it was desirable to employ as the voltage for the determination of the standard current a voltage which would occupy the same position on each characteristic. For example, it was not, and is still not, known with certainty whether there is a small variation of current with voltage on the flat parts of the curves. If there is any such change, the values of the relative currents would be affected by the value of the voltage at which it was decided to measure the standard saturation current. The method adopted ensures that there are no errors arising from considerations of this character, which would be appreciable in comparison with the unavoidable experimental error. In all the curves but two the original three-volt standard could be retained. In fact, it approximately satisfied the condition just described, the current at zero volts in these cases being on the rapidly rising part of the characteristic.

The relative currents thus obtained were then plotted for each series against the actual volts given by the voltmeter and the amount of displacement along the voltage axis was judged, which would be necessary to bring all the curves as nearly as possible to coincidence. This amount is, of course, in general different for the different curves, but is the same for every experimental point belonging to any one curve. The displacements are not applied to the curves, which constitute a secondary inference from the experimental data, but to the primary source of evidence, the experimental points themselves. The absolute position of the composite curve in relation to the scale of voltage is at present an entirely arbitrary matter, in default of any knowledge of the actual contact difference of potential K occurring in any single experiment. The displacements have, however, been so chosen as to bring the point A (fig. 4), formed by the intersection of a horizontal line through the standard saturation value unity and the dotted extension of the straight or slightly concave part FB of the characteristic, over the zero on the volt scale.

That the point A will not be far from that which corresponds to the condition of zero electric field between the two electrodes, *i.e.*, $V + K = 0$, might be anticipated on the following grounds. The data in fig. 3, and still more in fig. 4, indicate that there is no considerable direct effect of the applied field in helping the electron emission. In fact, I have frequently made explicit tests to see if the part DE of the curve slopes upwards, as appears to be suggested by the points in fig. 4, but I have never been able to convince myself that it does. Some experiments have given a small increase, some a small decrease, and others no change with rising voltage. This is a point which deserves further examination, but if there is any effect * of this kind it is certainly small. It is presumed, of course, that the voltages used in such tests are not such as to generate appreciable ionization in the surrounding gas. Inasmuch as the direct effect of the electric field is negligible, the curving of the part BCD of the characteristic is to be attributed to such secondary factors as the mutual repulsion of the electrons, electron reflection at the copper electrode, the return to the drop of some of the emitted electrons owing to collisions with gas molecules, and the effects of the holes in the copper sphere. Inasmuch as under ideal conditions in which the electron-emission or saturation current is very small, the vacuum is so high that gas collisions are negligible, there is no electron reflection at the receiving electrode, and the receiving electrode is a complete sphere, in the absence of electric field across the gap every electron once emitted from the drop will reach the copper sphere, because there is nothing to turn it back or to enable it to go elsewhere. Thus under such ideally perfect conditions the characteristic will consist of a flat saturation part AE intersecting with a part such as AFG, in which the emitted electrons are returned to the source by the opposition of the retarding field. This argument does not establish the coincidence of the point A with the zero potential difference, inasmuch as there is nothing *a priori* which enables us to foretell the shape of the part AFG. I have, however, succeeded in making independent experiments which determine, within limits, the contact difference of potential K and the characteristic curve for the chemical emission simultaneously. These experiments, which will be described later, fix the position of true zero volts somewhat to the left of the point A.

Fig. 4 shows the results of displacing the data along the voltage axis in the manner I have explained. The magnitudes of the displacement, and certain details which may

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* For a case in which there is a definite indication of diminishing currents with rising voltage on this part of the curve, see p. 25 *infra* (fig. 12).

be of importance relating to the different series of observations, are set forth in the following table and remarks :—

TABLE I.—$COCl_2$.

Number of series.	Mark indicating experimental points of series on curves.	Initial pressure, millimetres of Hg.	Final pressure, millimetres of Hg.	Displacement in volts from volt-meter readings to scale position in fig. 4.	Date.
I.	×	0·0015	0·016	+ 1·00	3/8/1916
II.	⊙	0·004	0·020	+ 1·45	25/7/1916
III.	▲	0·001	0·011	+ 0·55	25/9/1916
IV.	⊡	0·003	0·087	+ 3·30	2/11/1916
V.	⊕	0·002	0·012	+ 2·62	3/11/1916
VI.	•	0·001	0·038		16/9/1916

(The numerals I., &c., and marks ×, &c., are relevant to the data in figs. 3 and 5, as well as in fig. 4.)

Remarks on each Series.

I. ×.—Generator adjusted at the beginning of the experiment and later. The effect rose slowly after each adjustment. Chemical saturation current: minimum value 45 divisions per minute with cap. 0·01 mfd., maximum 200 divisions per minute, cap. 0·04 mfd. Saturation photo-electric current, 64 divisions per minute with 0·04 mfd. Maximum chemical and photo-electric effects thus of same order of magnitude. Gas was pumped out in the middle of these experiments without affecting the results. These observations were very consistent. The only apparent defect was a small insulation leak which had to be allowed for. The slight variability of this makes the point of intersection of the curve (I., fig. 3) and the voltage axis a little doubtful. A test at the end of the series with the mercury line 4355 gave 252 divisions per minute and with the green line 0·7 division per minute, the capacity being 0·01 in each case.

II. ⊙.—Generator adjusted at the beginning and again at the middle of the series. Effect rose before and after adjustment. Maximum chemical saturation current, 160 divisions per minute, minimum 42 per minute; λ 4355 photo-electric saturation current, 160 divisions per minute; all with capacity 0·02 mfd. Six drops per minute, diameter of drops 3 to 4 mm.

III. ▲.—Generator not adjusted in these experiments. Chemical effect dropped steadily most of the time, then rose a bit towards the end and fell off again. Chemical saturation current: maximum 28 divisions in 60 seconds, capacity 0·03 mfd.; minimum 37 per minute, capacity 0·01 mfd. λ 4355 photo-electric saturation, 53 per minute with 0·03 mfd. capacity. Four drops in 90 seconds.

IV. ⊡.—Generator adjusted twice. Chemical effect rose after first adjustment. After second it fell, then rose again. It was large most of the time. Chemical saturation current: maximum 700 divisions per minute with capacity 0·04 mfd., minimum 7 divisions per minute with capacity 0·01 mfd. There was no detectable photo-electric current with $\lambda = 4355$ in this experiment. An effect equal to about 1 per cent. of the chemical emission should have been detected. Considerable gas pressure was present, and there may have been a small air leak into the apparatus. Six drops per minute.

V. ⊕.—No adjustment of generator in this series. Chemical effect small but very steady, only varying between 26·5 and 31·5 divisions per minute with 0·01 mfd. capacity: photo-electric λ 4355 saturation, 300 divisions per minute with 0·01 mfd.

VI. •.—No adjustment of generator. Chemical saturation current rose gradually from 18 to 268 divisions per minute with 0·01 mfd. and then fell to 120 per minute. Photo-electric 4355, saturation current 240 divisions per minute with 0·01 mfd.

An examination of the foregoing remarks shows that the series of observations I. to V., which are comprised in fig. 4, embrace a wide variety of conditions. Thus the saturation chemical current is varied over the range from 700 divisions per minute with 0·04 mfd. or $8 \cdot 2 \times 10^{-10}$ amperes to 7 divisions per minute with 0·01 mfd., or $2 \cdot 05 \times 10^{-12}$ amperes. The photo-electric saturation currents under practically the same illumination in each case varied between the limits $8 \cdot 8 \times 10^{-11}$ amperes and something under

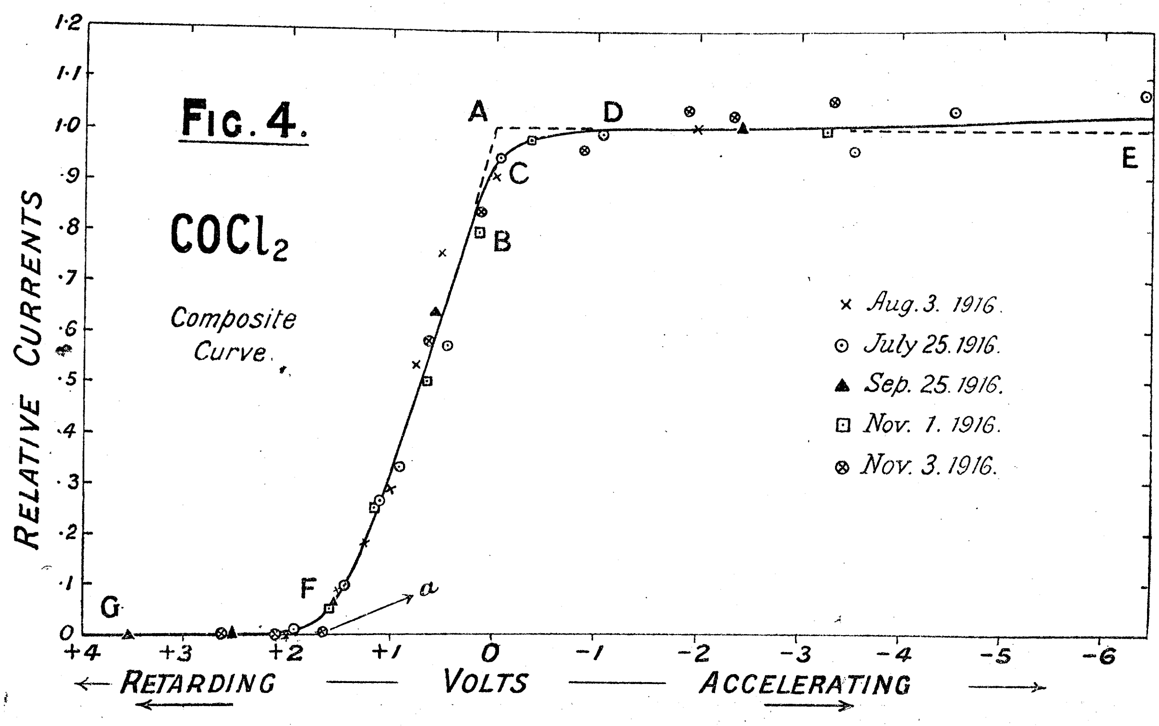


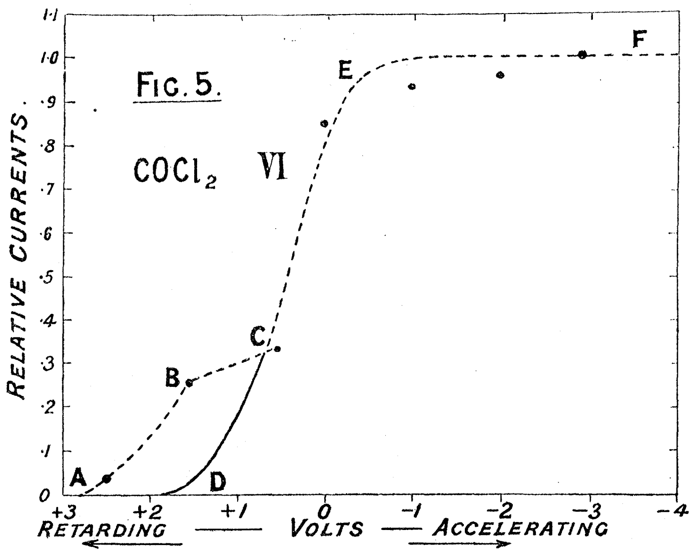
FIG. 4.

3×10^{-13} amperes. The pressure of gas in the apparatus covered the wide range from 0·001 mm. to 0·087 mm. In the different series the chemical saturation currents rose or fell with time or did each of these alternately. In one series it was almost constant. In one case the standard photo-electric current was 10 times as great as the standard chemical current, in another it was less than 1 per cent. of it, whilst in another case these currents were about equal. The number of drops per second varied between 1 in 10 seconds and 1 in $22\frac{1}{2}$ seconds, possibly more. The size of the drops probably varied also.

In spite of these wide changes in the conditions, all the points in fig. 4 fall close to the continuous curve drawn. It is not certain that they are not all coincident with this curve within the limits of likely experimental error, with the single exception of the observation marked *a*. An examination of the data makes it practically certain that the electrometer was not functioning when this observation was taken, as the photo-electric observation immediately following it also gave a zero deflection when it should have given a measurable deflection according to the run of the rest of the photo-electric curve.

The coincidence of the points with the smooth curve in fig. 4 proves that this curve gives, approximately at any rate, the true shape of the $COCl_2$ characteristic, and confirms the suspicion that the moving about along the volt axis, as in fig. 3 of the experimental curves, is due to changes in the contact potential between the surfaces.

The plot of VI. • did not agree with series I. to V., and is not included in fig. 4, but is shown separately in fig. 5, together with a copy DEF of the composite curve in fig. 4 shifted 0·25 volt to the right of its position in that diagram. In this experiment the points to the right of + 1 volts were taken first and the others later. It will be seen that the first five points taken agree with fig. 4, but the later points would have to be given a different displacement to bring them on to the common curve. This seems a



clear indication of a change in the contact potential difference between the surfaces taking place during the course of a single set of observations.

§ 3.—*The Characteristic Curves for Chlorine.*

The manipulation in the case of chlorine was very similar to that in the case of $COCl_2$ and the results are of the same general character. Two typical characteristics as actually determined are shown in fig. 6. The curves show a flat saturation part for accelerating voltages exceeding about four. There is the same tendency to haphazard displacements of the curves parallel to the voltage axis as in the case of $COCl_2$. The magnitude of this displacement seems, however, to tend to be smaller with chlorine, the maximum separation I have observed in six characteristics taken with this gas being 0·95 volt. The fact that the two curves shown in fig. 6 do not appear to be parallel is due to the distortion caused by the different vertical scales. The standard current has the arbitrary value 1·09 in one case and 0·95 in the other.

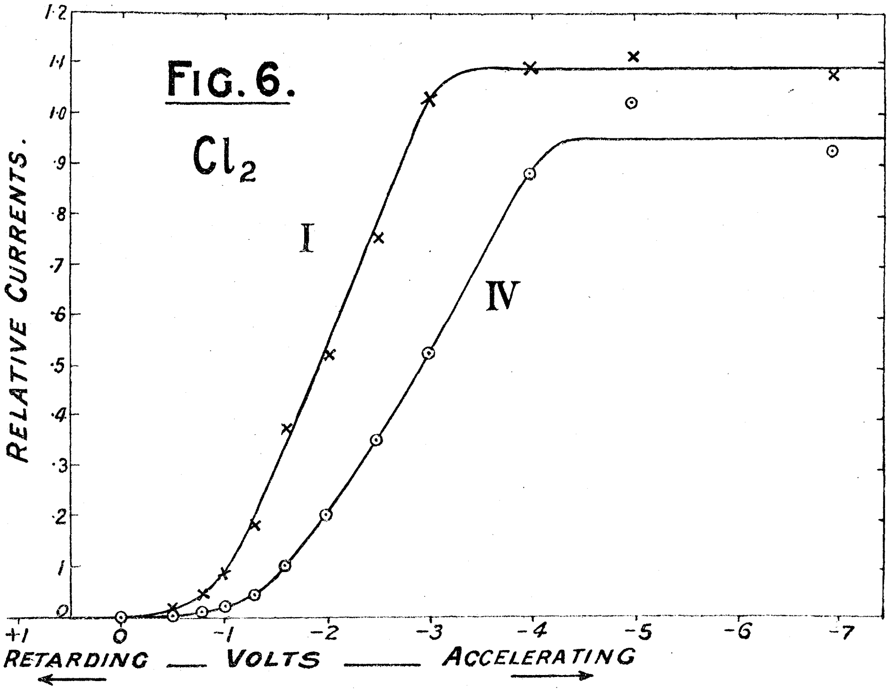


FIG. 6.

Cl_2

As in the case of $COCl_2$, the various series have been reduced to unit saturation current and displaced by varying amounts along the vertical axis to form a composite curve. The various data referring to the relevant experimental series are given in the following table and remarks ;—

TABLE II.—Cl_2.

Number of series.	Mark indicating experimental points of series on curves.	Initial pressure, millimetres of Hg.	Final pressure, millimetres of Hg.	Displacement in volts from volt-meter readings to scale position in fig. 7.	Date.
I.	×	0·003	0·080	0·00	20/4/1917
II.	⊙	0·002	0·052	— 0·10	22/4/1917
III.	▲	0·002	0·002	— 0·25	22/4/1917
IV.	⊡	0·002	0·040	— 0·55	22/4/1917
V.	⊕	0·003	0·100	— 0·70	17/4/1917
VI.	•	0·002	0·080	+ 0·25	25/4/1917

[The numbers I., &c., refer to the curves in fig. 6 as well as fig. 7.]

Remarks on each Series.

I. ×.—No adjustment of generator. Chemical saturation current increased uniformly and slowly from about 200 divisions per minute to about 800/min. and photo-electric (4355) saturation current equal to about 100/min., all with additional capacity 0·01 mfd. Pump stopped and gas allowed to accumulate.

II. ⊙.—No adjustment. Chemical saturation current increased slowly from 310/min. to 508/min., photo-electric 60/min., all with 0·01 mfd. Pump stopped and gas accumulating. One drop per minute.

III. ▲.—No adjustment. Chemical saturation current increased slowly from 10/min. to 15/min., and then towards the end rose rapidly to 300/min.; photo-electric 12/min.; all with 0·01 mfd. In this series the chlorine was kept immersed in liquid air and the pumps running continuously. One drop per minute.

IV. ⊡.—No adjustment. Chemical saturation current increased slowly from 250/min. with 0·02 mfd. to 500 per minute with 0·04 mfd., photo-electric 18/min. with 0·02 mfd. Pump shut off and gas accumulating. One drop in 110 seconds.

V. ⊕.—Chlorine generator shut off from apparatus and effects presumably due to chlorine adsorbed in the apparatus. Chemical saturation current fell slowly, the measured limits being 135/min. and 97/min. with 0·000121 mfd., but this difference is partly exaggerated by errors of measurement. Photo-electric 370/min. with 0·000121 mfd. Pump shut off and products accumulating. Six drops per minute.

VI. •.—Chlorine generator shut off and other arrangements as in V. ⊕. Chemical saturation current rose slowly from 209/min. to 258/min. with 0·000121 mfd. Photo-electric (4355) saturation current 1300/min. with 0·000121 mfd. One drop in 110 seconds.

These data show that the experimental conditions under which chlorine has been tested cover a wide range as in the case of $COCl_2$. Thus the chemical saturation current is varied between the limits 500/min. with 0·04 mfd., equal to $5 \cdot 9 \times 10^{-10}$ amperes, and about $3 \cdot 5 \times 10^{-13}$ amperes. The photo-electric saturation current varies between about 3×10^{-11} amperes and 10^{-12} amperes. The chemical emission increases and decreases with time in the different series; sometimes it is almost constant, at others it is changing rapidly. The pressure of gas in the apparatus ranges from 0·002 mm. to 0·100 mm. The chemical effect is nearly 60 times the photo-electric in one series, whereas it is only about one-sixth of the photo-electric in another, and this ratio has intermediate values in other cases. In five of the series the gaseous products of the reactions occurring were allowed to accumulate, whereas in one of them the pumps were run continuously. The rate at which the drops fell was varied between 1 in 10 seconds and 1 in 110 seconds.

In spite of this wide variation in the conditions, all the points fall on the smooth curve in fig. 7 to the degree of accuracy which it seems reasonable to expect. An exception is perhaps furnished by the 3 points × of series I. at − 2·5, − 3 and − 4 volts.

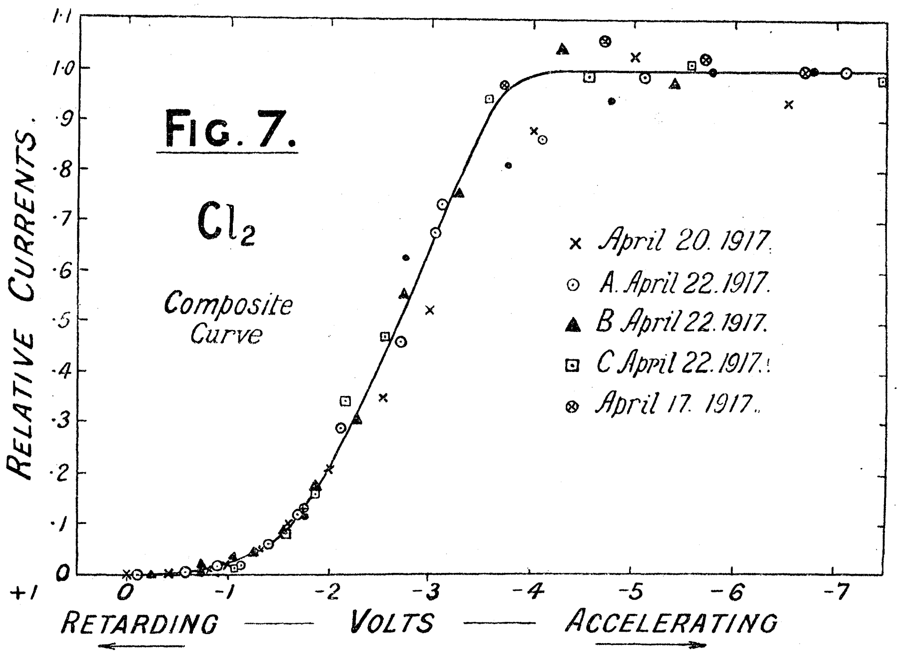


FIG. 7.

It is unlikely that chance errors, which would have to be rather large in any event, would make these three points, which were determined in succession at the beginning of the series, lie so persistently to the right of the graph required by the rest. It seems likely that we have here another example of a change in the contact potential taking place during the actual course of the experiments, as in the case of series VI. with $COCl_2$. Some of the points in I. ×, II. ⊙, and VI. ● might seem to suggest a slower voltage approach to saturation than the normal, and it was thought that this effect might be

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attributable to the rather high gas pressures which developed in these experiments. The fact that III. ▲, in which the pressure was kept down to 0·002 by operating the pumps continuously, does not show this tendency, would seem rather to support such a contention. An examination in detail of the data, however, is against it. For example, in I. × and VI. • the currents at the high voltages were measured at the lower pressures and in II. ⊙ conversely. On the whole it seems likely that any such appearance is illusory and, except in the case of I. ×, where a displacement caused by change in contact potential during the series seems probable, due to chance errors.

It appears, then, that fig. 7 determines the shape of the chlorine characteristics. No determination of the contact potential with chlorine present has yet been made, so that the true zero on the volt scale in fig. 7 cannot yet be assigned with certainty. All that can be said at present is that an examination of the relative positions of the chemical and of the photo-electric curves which were taken at the same time shows that the true zero of fig. 7 lies to the right of — 2·2 volts.

§ 4.—*Hydrochloric Acid.*

The effects given by this gas are of a much smaller magnitude than those given by carbonyl chloride and by chlorine. It was impossible to make accurate measurements of them with the apparatus used with the latter gases, and such fragmentary data as were obtained only enable qualitative statements to be made. The characteristics appear to be similar generally to those given by the other gases, and to drop from saturation to zero current within a range comparable with one volt.

§ 5.—*The Characteristic Curves for Water.*

These experiments were made in 1915 with an apparatus which differed in some details from that shown in fig. 1 and used in the experiments described up to this point. Instead of the glass tube ABC of fig. 1, the alloy was fed into the testing vessel through a copper tube fitted with a tapered silver nozzle. This had a fine hole bored vertically down the centre and was screwed on to the copper tube. The other electrode was 7·5 cm. in diameter. The alloy used was also different, having the composition NaK instead of NaK_2. The electrometer sensitiveness was 540 divisions per volt and the capacity of the electrometer and connections 0·00032 mfd. There is an element of doubt about the correctness of the voltmeter set up which was used in some of these early experiments, and I am only prepared to state the applied potential differences as relatively correct. The units are probably volts, but they may be as small as 0·6 volt. The data for the series of observations which were completed are given in fig. 8, and some of the details in Table III. and in the remarks which follow.

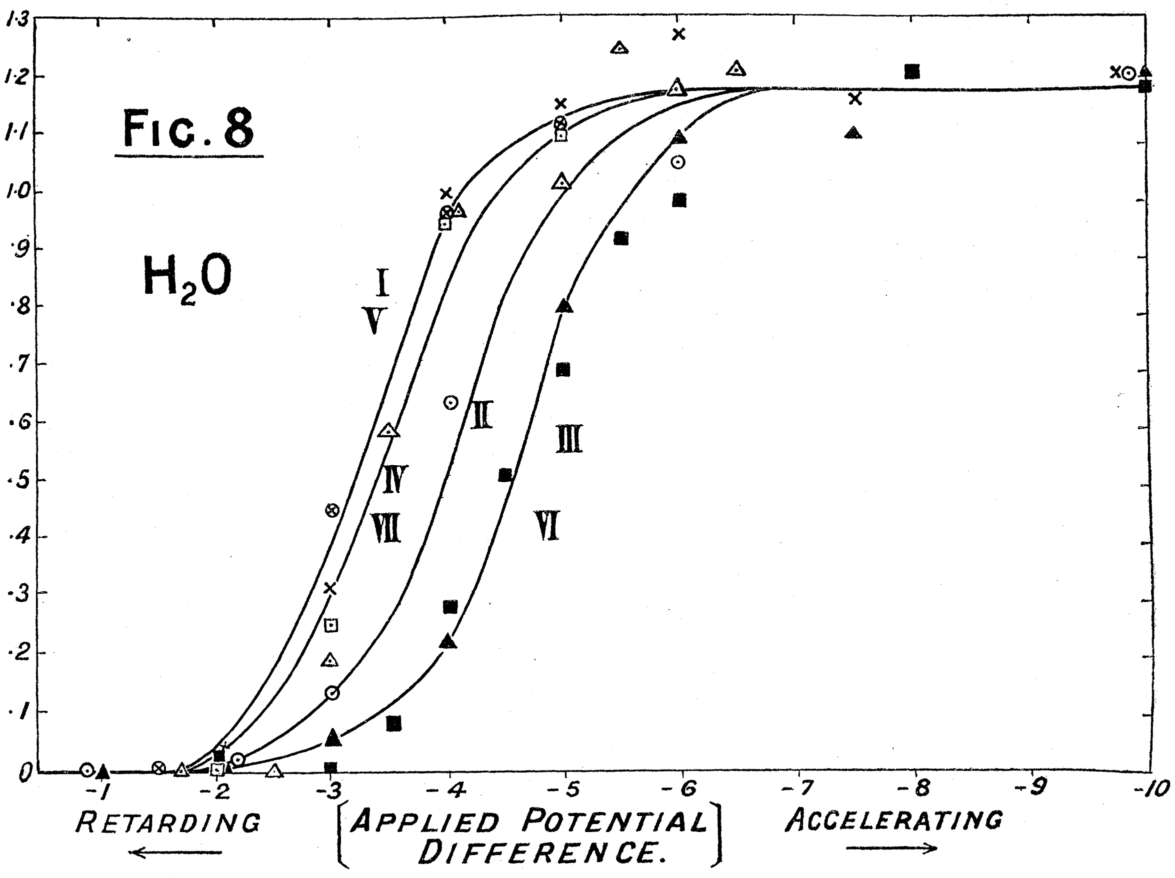

FIG. 8

TABLE III.—H_2O.

Number of series.	Mark indicating experimental points of series on curves.	Displacement on voltmeter scale from voltmeter readings to scale position in fig. 9.	Date.	Page of notebook.
I.	×	− 1·15	1915	Vol. 1, p. 77
II.	⊙	− 0·75	1915	,, ,, p. 74
III.	▲	0·00	1915	,, ,, p. 68
IV.	⊡	− 1·00	1915	,, ,, p. 55
V.	⊕	− 1·30	1915	,, ,, p. 54
VI.	■	+ 0·05	6/8/1915	,, 2, p. 52
VII.	△	− 1·00	13/8/1915	,, ,, p. 58

[The numbers I., &c., and marks ×, &c., refer to figs. 8 and 9 equally.]

Remarks.

The gas was not allowed to accumulate, but the pumps were kept running continuously in all these experiments. The gas pressure is not recorded, but probably it did not much exceed 0·002 mm. at any time. In V. ⊕ the water vapour was obtained by placing crystals of $CaCl_2$ $6H_2O$ in the generating tube and immersing it in ice. In IV. ⊡ the same crystals were used but the container was immersed in a mixture of ice and salt. In all other cases mixtures of sulphuric acid with different suitable proportions of water were used, and the mixture was kept at the temperature of the room. In VII. ◬ equal parts of the two liquids were taken. The water vapour was given off quietly and the liquid did not boil. In I. to V. the drops fell at the rate of about one per minute, in VI. at the rate of seven per minute. After VI. a large structure with a wart-like appearance had grown on the end of the nozzle, and in VII. the globules came out of this structure. They were very large and looked dirty when attacked by the H_2O. In the previous experiments, in which much larger currents were obtained, the oxidised layer either looked quite white or was invisible. It was noticed that the oxidised metal showed no appreciable photo-electric effect with the quartz mercury lamp except just when the oxidised skin broke and the bright metal shone through. In series I. to V. the electrometer deflections were reduced by adding suitable capacity from an adjustable air condenser. The added capacities are not recorded in these cases. In VI. 0·2 mfd. was added from a standard condenser and the maximum saturation current was about 50 divisions per minute. In VII. the capacity was that of the apparatus alone (0·00032 mfd.) and the saturation current was 50 divisions per minute in this case also. VI. and VII. probably correspond respectively to the largest and smallest effects dealt with.

In fig. 8 the individual data I. to VII. are plotted as they were experimentally determined. The points for I. × and V. ⊕ fall so close together that they appear to fall on a single curve. The same applies also to each of the pairs IV. ⊡, VII. ◬ and III. ▲, VI. ■. Thus the seven sets of data appear to fall on four distinct curves. However, these curves are all nearly parallel to one another, just as was the case with the curves for $COCl_2$ and Cl_2. They have therefore been subjected to the same treatment, namely, given the arbitrary displacements which are recorded in Table III. parallel to the volt axis. The result is shown in fig. 9. It will be seen that, with the exception of the points marked *a*, *b* and *c*, all the points then lie on a single smooth curve to within the degree required by the probable experimental errors. Of the excepted points, *b* is doubtful owing to a rapid variation of emission with time when it was taken, and *a* and *c* should not, except for the sake of having a complete record of the observations, have been included in the diagram, as they are determined by minute deflections comparable in magnitude with the variations in the natural leak of the electrometer system in this particular experiment.

Fig. 9 shows that the form of the characteristic curve for H_2O is of the same general nature as those for Cl_2 and $COCl_2$. No determinations of the contact potential K with water present have been made, so that the position of the true zero of potential difference on fig. 9 is uncertain.

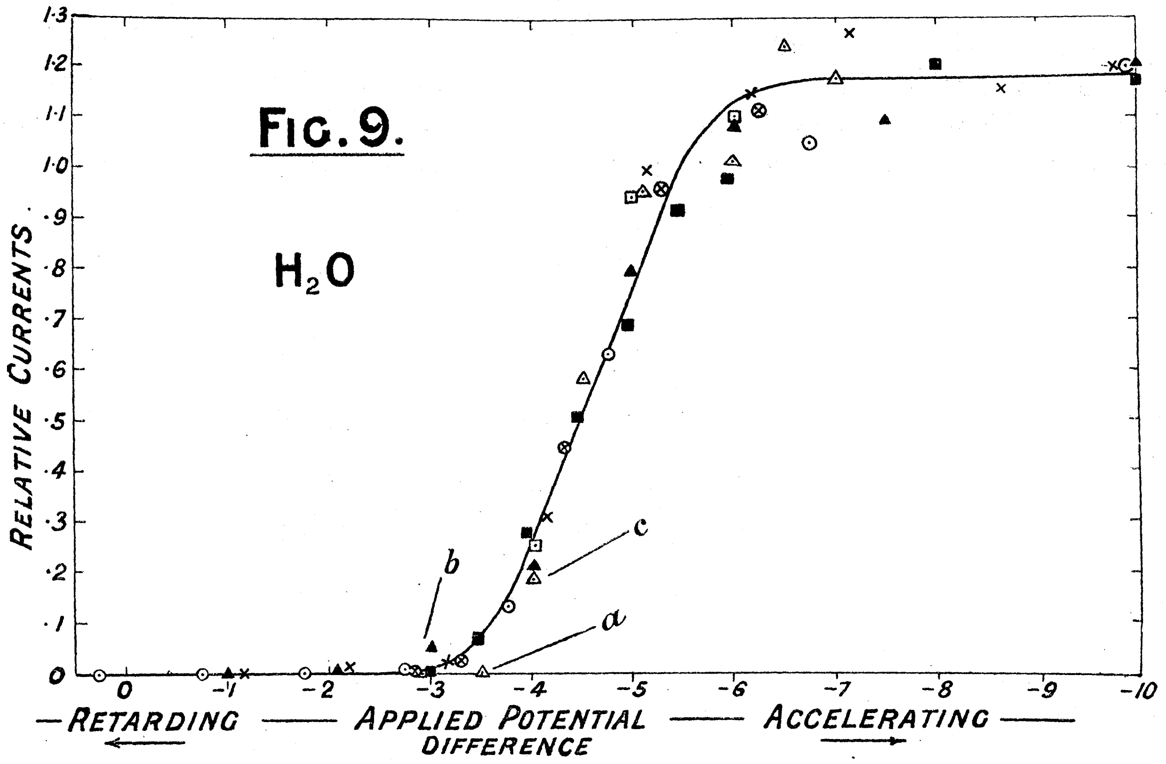

Fig. 9.

§ 6.—*Location of Zero on the Volt Scale for $COCl_2$.*

A knowledge merely of the shapes of the characteristic curves does not enable us to say much very positively about the kinetic energy of the liberated electrons, owing to the uncertain and changeable contact potential difference. In fact, it is necessary to find the position on the volt scale which corresponds to zero electric field between the electrodes, either by a determination of the contact potential difference for some particular case or by something which is equivalent to this. In principle the position of the zero on the volt axis can be found from a study of photo-electric data. Experiments by the writer and Prof. K. T. Compton,* in which a structure similar to that used in the preceding experiments was employed, namely, a small photo-electric source at the centre of a large spherical electrode, have shown that the photo-electric characteristic curves have the form shown in fig. 10. They consist of a flat part AB joined to a sloping part such as AC or AD, whose slope diminishes with diminishing wave-length of the monochromatic exciting light. The sloping portions all converge to a common point A of the saturation part of the characteristic independently of the wave-length used. A is the position of the true zero of potential difference, and, in fact, these small currents are completely saturated in any accelerating electric field, however small. Thus one method of locating the zero would be to find the convergence point A to the saturation value of different monochromatic characteristics such as CA, DA. This would, of

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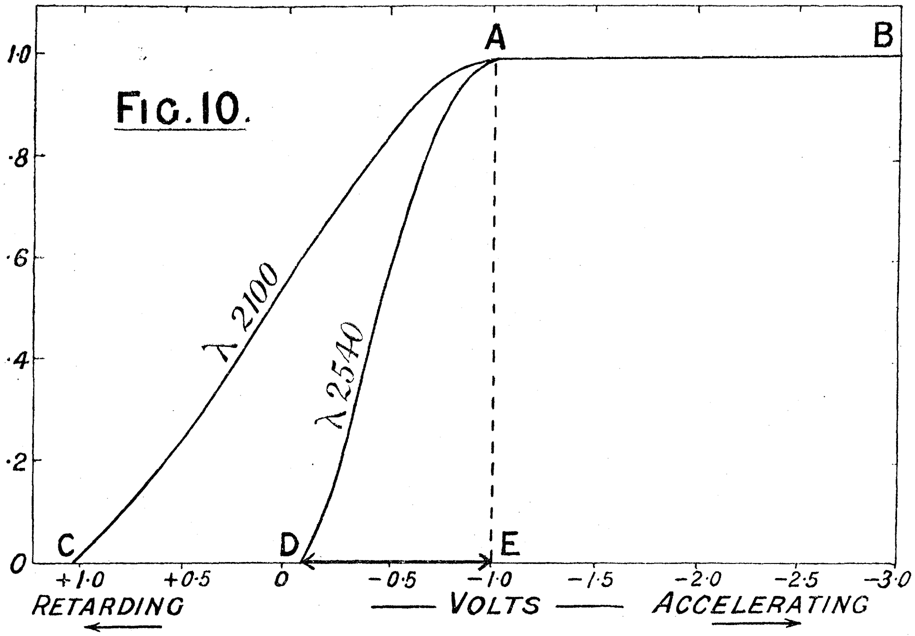
* 'Phil. Mag.,' vol. 24, p. 575 (1912).

course, have to be done simultaneously with the measurements of the chemical emission, and an examination of the preceding data will show that it is hopeless to attempt to determine this point accurately under these conditions. For it is just as the currents approach the maximum value that the absolute errors become largest and the exact location of the points becomes most difficult. This difficulty can be avoided if we can make an auxiliary determination of ν_0 the threshold frequency of the light which is just high enough to excite any photo-electric emission at all. For if D is the point where the foot of a characteristic such as DA for some particular frequency ν cuts the volt axis and DE is denoted by V, then

FIG. 10.



$$eV = h(\nu - \nu_0)$$

where e is the charge on an ion, h is PLANCK'S constant and e and V are in the same absolute units. By using very large photo-electric currents, points such as D can be determined with great accuracy and comparative ease, whereas increasing the magnitude of the emission does not diminish the inaccuracies to which determinations of points like A are liable.

Data to which this second method can be applied were obtained in connection with the Series I. × $COCl_2$ of 3/8/1916 (p. 12). Observations at the end of this series showed that with the blue filter the photo-electric saturation current was 248 divisions per minute, and that with the green filter it was only 0·6 div./min. At the same time the chemical saturation current was 4·0 divs./min., a capacity of 0·01 mfd. being included in each of these measurements. The pressure of the reaction products had risen to 0·016 mm. at this stage. The fact that the blue light of wave-length 4347–4358 and frequency $6 \cdot 89 \times 10^{14}$ gave a large deflection shows that this frequency was considerably higher than the threshold value. If the small value of the current with λ 5460, frequency $5 \cdot 49 \times 10^{14}$ could be relied on as genuine, it would establish ν_0 as very close to λ 5460 and just on the low-frequency side of it. On the other hand, if this small deflection is spurious or due to a trace of light of higher frequency mixed with the λ 5460, the threshold value must be well on the low-frequency side of λ 4350 on account of the large deflection given by λ 4350. This experiment shows that ν_0 was somewhere between $5 \cdot 49 \times 10^{14}$ and $6 \cdot 89 \times 10^{14}$ at this stage. A plot of the photo-electric data got during series I. × shows that the photo-electric current with λ 4350 met the voltage axis at $-0 \cdot 20$ volt. This was immediately below the point at which the chemical current attained $0 \cdot 50$ of its saturation value. Taking the frequency as $6 \cdot 89 \times 10^{14}$ for λ 4350 and $5 \cdot 49 \times 10^{14}$ for λ 5460, the value of $(\nu - \nu_0) h/e$ is $0 \cdot 58$ volt for $\nu_0 = 5 \cdot 49 \times 10^{14}$ and zero for $\nu_0 = 6 \cdot 89 \times 10^{14}$. Thus the true zero must lie between a point which is coincident with the $-0 \cdot 20$ volt on the voltage scale and with the 50 per cent. point on the chemical characteristic and a point which is $0 \cdot 58$ volt negative to these points. At this period the contact potential difference between the two electrodes then was between $0 \cdot 2$ volt and $0 \cdot 78$ volt, and the true zero between the points where the chemical current had attained between $0 \cdot 50$ and $0 \cdot 86$ of its saturation value. Comparing with the composite curve in fig. 4, this makes the true zero lie between $+0 \cdot 12$ and $+0 \cdot 70$ volt on that diagram. It must be definitely to the right of $+0 \cdot 70$ on account of the large deflections given by λ 4355, but how far to the right these data do not determine.

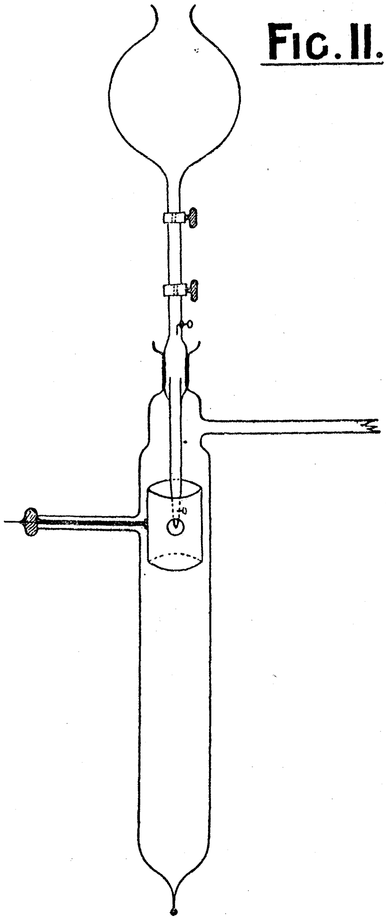


FIG. II.

The importance of fixing this zero led me to make a renewed attack on this part of the problem recently. For success in this determination it is necessary to have a series of intense sources of monochromatic radiation not too far apart on the frequency-scale. It is also necessary to carry out the successive measurements with the utmost rapidity. By this time the apparatus shown in fig. 1 had come to grief and a new testing vessel of simpler construction, shown to scale in fig. 11, was employed. Apart from the smaller dimensions, the principal change consists in the substitution of a cylindrical copper electrode, 2 cm. in diameter, instead of a spherical one. The alloy used was NaK_2 and the $COCl_2$ was the KAHLBAUM specimen already referred to. The monochromatic sources were the lines of the mercury arc spectrum projected on to the drops by a Hilger glass monochromatic illuminator, Some useful data pertaining to the lines used are collected in the following Table :—

TABLE IV.—*Mercury Spectrum (visible).*

Colour.	Wave-length between (cm. × 10^5).	Frequency (per second).	Relative intensity.*
Yellow	5·769 and 5·790	5·19 × 10^{14}	23·6
Green	5·460	5·49 × 10^{14}	18·7
Blue	4·916	6·10 × 10^{14}	1·0
Violet 1	4·347 and 4·358	6·89 × 10^{14}	14·7
Violet 2	4·046 and 4·077	7·40 × 10^{14}	8·2

In addition to the illuminator, I had the use of a large selection of colour filters kindly lent by Messrs. Hilger. Unfortunately, those which might have been useful cut down the working radiation too much. For monochromatism the dispersion of the illuminator has therefore alone been relied on. As a matter of fact, the lines were all sharp and widely separated, and no trouble has been experienced, owing either to overlapping or to stray light of other wave-lengths. The lamp was run at the maximum brightness at which it could be depended on to run smoothly and remain constant. To prevent trouble due to stray light it was necessary to enclose the lamp in a large tin box, and to prevent over-heating a water-cooling system had to be provided. Once the apparatus was adjusted the successive lines could be rapidly thrown on the drops simply by adjusting the screw setting of the illuminator. In every case the satisfactoriness of the mechanical setting was confirmed by visual observation.

Very steady conditions have been obtained with these arrangements. The data for two determinations of the characteristic curves with this apparatus are shown in fig. 12. One of these, ×, was taken the same day as and immediately preceding the determination of the true zero to be described in a moment, and the other, ⊙, as early as possible the following day. The smooth curve is drawn to the first set of points marked ×, and will be seen to cover them very closely. The first set marked × agree with the second, except that (1) they lie about 0·12 volt to the right, indicating a change by this amount in the contact potential difference between the two experiments, and (2) they give higher values for the small currents at the foot of the curve on the left-hand

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* These energy measurements are taken from a paper by E. S. JOHANSEN in 'Strahlentherapie,' vol. 6, p. 55 (1915), and are for a different design of lamp which ran on 220 volts, taking 2·6 amperes with 128 volts between the poles of the arc. The quartz mercury vapour lamp used in these experiments ran on 200 volts and took 3·0 amperes with 150 volts between the poles. No doubt the relative intensities of the lines will vary to some extent with different installations, but for the present purpose it is only necessary to know the relative energies approximately.

side. These small currents are important, and the collective data bearing on them will be considered later. An examination of the experimental conditions on which the results plotted in fig. 12 are based shows that the values denoted by ⊙ are here liable to much more serious errors than those denoted by ×, which therefore are alone relied on in obtaining this part of the curve. The numbers written alongside the points marked ⊙ indicate the order in which these points were determined. It should be mentioned that point 1 is unreliable owing to a very rapid change in the standard current when it was determined.

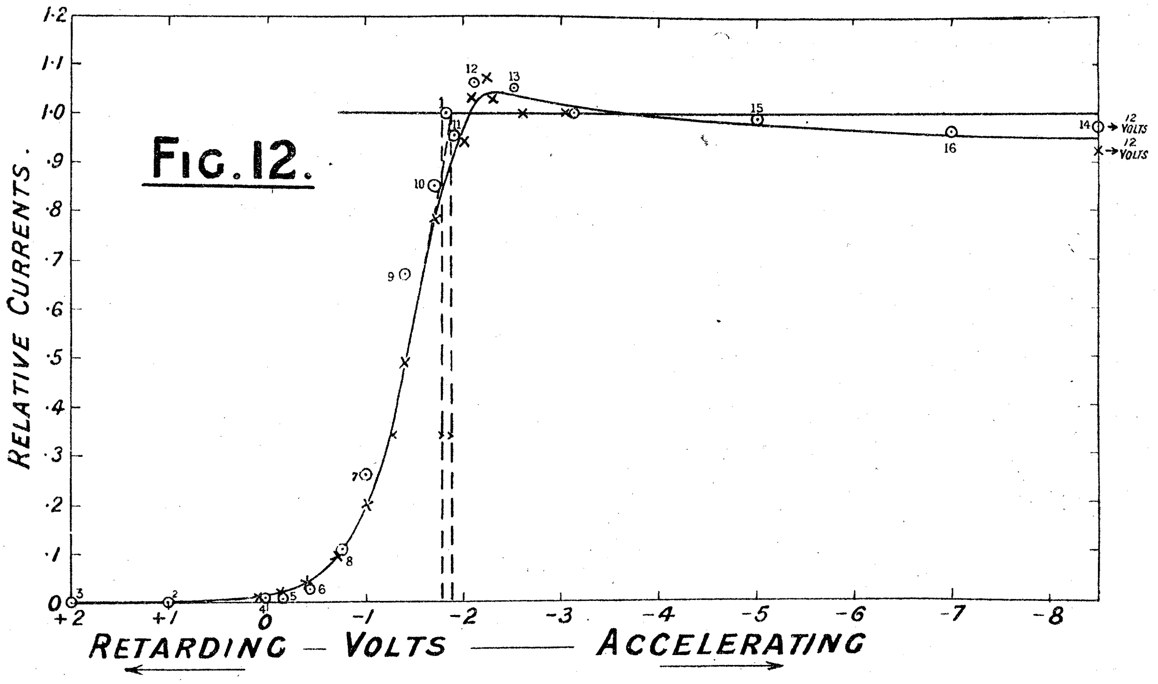

FIG. 12.

The second series of points indicate a small but definite falling off in the saturation currents with rising potentials. This may be due to some bias of chance errors, but it does not seem likely to be, as the data for the first series also support it. There is no evidence of such an effect in the $COCl_2$ data for the spherical electrode plotted in fig. 4, but it may be masked by the errors of observation. In fact, the experimental data which look most reliable for this part of the curve point to a rising current with rising negative voltages in those experiments. On the other hand, although the matter was not explicitly tested at the time the experiments were made, the chlorine data which form the basis of fig. 7 show, on re-examination, a distinct drooping tendency towards higher voltages. The evidence is thus not clear that this tendency is peculiar to the cylindrical anode. It may be illusory, but that is unlikely. It may be a general effect present with the spherical electrodes, but masked by errors. There are several physical effects which the electric field might exert on the drops which might give rise to such a phenomenon.

Apart from the hump near — 2 volts, the characteristic in fig. 12 is not very different from that in fig. 4. The horizontal stretch from the 50 per cent. point to the 1 per cent. point is for fig. 12, ×, 1·40 volts, as compared with the value 1·20 volts of the stretch from the 50 per cent. to the 1 per cent. point for the curve in fig. 4. On the other hand, the stretch from the 90 per cent. to the 50 per cent. point in fig. 12 is only 0·46 volt, whereas it is 0·65 volt in fig. 4. The total stretch from the 90 per cent. to the 1 per cent. point is practically the same in both cases, the difference between the two curves being that fig. 12 is relatively steeper near the top. The data in fig. 12 are only relied on to give the shape of the characteristic. It is not supposed that the relative currents and voltages had these values when the photo-electric data were being determined. The instantaneous values of the relative chemical currents were determined at the same time as the photo-electric data.

In taking the data in fig. 12 the pressure in each series was less than 0·001 mm. at the beginning and equal to 0·004 mm. at the end.

The determination of the threshold frequency ν_0 was carried out immediately after the series × of fig. 12 was completed, the pressure in the apparatus being 0·0045 mm. The measurements are shown in the following table, — 3 being used for the saturation voltage :—

TABLE V.

Nature of light used.	Electrometer deflection in scale divisions per minute.	Additional capacity microfarads.	Deflection due to light.	Deflection per unit light energy.
No light.	47	0·01		
λ 4055	162	0·01	116	14·15
No light.	45	0·01		
λ 4355	160	0·01	117·5	8·00
No light.	40	0·01		
λ 4916	39	0·01	0·5	0·5
No light.	37	0·01		
λ 5460	35	0·01	— 0·5	— 0·027
No light.	34	0·01		

The deflections in the second column when no light was used are due to the chemical effect which was falling slowly and steadily during these experiments. The values in the fourth column are got by subtracting the instantaneous chemical effect (got by taking the means of the preceding and following measurements) from the combined effect due to light and chemical action when the light is on the drop. The values in the last column are got by dividing those in the fourth column by the relevant energy data given in Table IV.

The deflections per unit-light energy are plotted against the frequency of the exciting light in fig. 13. According to measurements of the writer and K. T. COMPTON,* curves plotted from such data intersect the frequency axis at the threshold frequency ν_0. If we assume the half-millimeter deflection with λ 4916 to mean something, this fixes the position of ν_0 at the point A or $6 \cdot 02 \times 10^{14}$. On the other hand, if the reading at λ 4916 is disregarded, it follows from a consideration of the λ 4055 and λ 4355 points alone that the intersection cannot lie to the right of the point B or $6 \cdot 25 \times 10^{14}$, which is the point where a straight line through these two points meets the axis. Thus this experiment establishes the value of ν_0 as lying between the limits $6 \cdot 02 \times 10^{14}$ and $6 \cdot 25 \times 10^{14}$. It is unfortunate that the line λ 4916 is so weak, otherwise these limits could be narrowed very considerably.

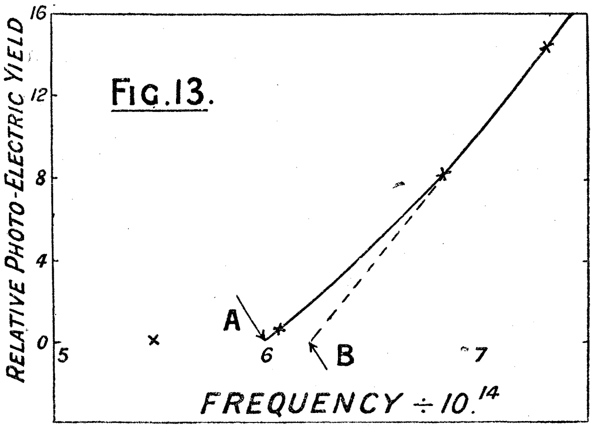
FIG. 13.

Immediately after determining ν_0 the measurements for determining the intersection of the photo-electric characteristic for the line violet 2 (λ 4046 to 4077) with the voltage axis were taken. The pressure was still 0·0045 mm. The photo-electric currents, in scale divisions in 60 seconds with 0·01 mfd. additional capacity connected with the electrometer, were as shown in the following table in the order in which the points were taken:—

TABLE VI.

Volts . . .	— 3	— 1·8	— 1·0	— 1·2	— 1·1	— 1·3
Current . . .	112	101	0·5	12	3	29·5

These data are plotted in fig. 14, from which it will be seen that the photo-electric characteristic for frequency $7 \cdot 40 \times 10^{14}$ cuts the voltage axis at — 1·07 volts. Thus the true zero on the volt scale *at this time* was $-(1 \cdot 07 - h/e\,(\nu - \nu_0))$, where $\nu = 7 \cdot 40 \times 10^{14}$ and $h/e, = 4 \cdot 124 \times 10^{-15}$, is expressed in appropriate units to give volts. Now $h/e\,(\nu - \nu_0)$ is equal to ·569 or ·474 volt, according to which of the limiting values of ν_0 determined above we take. Adding 1·07 to these, it follows that

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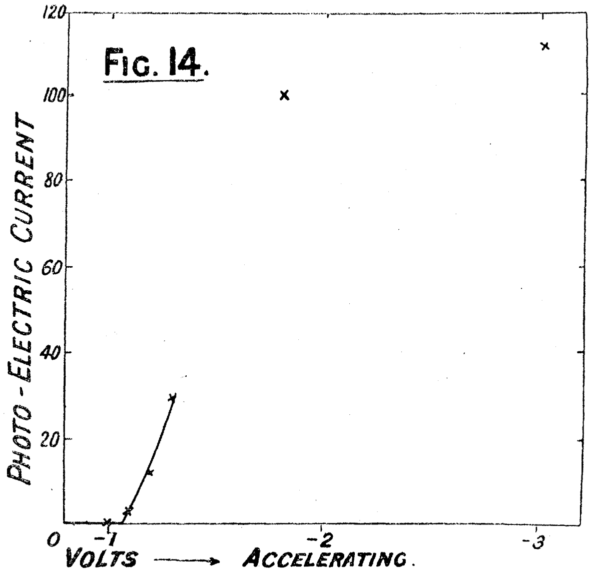
* 'Phil. Mag.,' vol. 26, p. 562 (1913).

we have ascertained the position of the true zero at that time as lying between the limits — 1·544 and — 1·639 volts.



The next point is to ascertain what was the position at that time of the chemical characteristic curve in relation to the volt scale used. Relevant chemical data were taken at the same time as the photo-electric data given in Table VI. An examination of these data shows that with — 1·00 volts the chemical current was then 34 per cent. of its saturation value at — 3 volts. It follows that for any $COCl_2$ characteristic curve for this apparatus the true zero will lie between the limits of 0·54 and 0·64 volts to the right of that voltage for which the current is equal to 34 per cent. of the saturation value. Applying this to the curve, points thus :— ×, in fig. 12, the two limiting values are given by the two broken vertical lines at — 1·78 and — 1·88 volts respectively. The inclined broken line represents the tangent to the characteristic at the point of inflection. It will be seen to intersect the horizontal line through the unit 3-volt saturation current value at the same point as the vertical line through the right-hand zero limit, to the accuracy within which the lines can be drawn. Thus the true zero lies between the intersection of the tangent at the point of inflection and the horizontal saturation current line and a point one-tenth of a volt to the left of this intersection.

These results support the conclusions already drawn from less complete data in the experiments with the spherical anode. In that case the true zero was only located to within 0·58 volt, but it was definitely placed to the left of the corresponding intersection. It therefore seems reasonable to assume that either with spherical or cylindrical anodes the true zero in this potential scale lies a fraction of a volt to the left of the point of intersection of the tangent at the point of inflection with the horizontal saturation line. Considering the nature of the experiments, the location of this zero to a higher degree of accuracy than one-tenth of a volt would obviously be a matter of some difficulty.

The data now under consideration clearly determine the contact differences of potential ruling between the electrode surfaces during the experiments. If v is the velocity with which the electrons reach the receiving surface, V the retarding potential recorded by the voltmeter, K the contact potential, then for illumination by light of frequency ν of a source whose threshold frequency is ν_0, in general,

$$\tfrac{1}{2}mv^2 = h(\nu - \nu_0) - e(\mathrm{V} + \mathrm{K}).$$

At the intersection of a curve such as that in fig. 14 with the volt axis, V is just sufficiently great to reduce v to zero. Calling this value of V, V_0, clearly

$$\mathrm{K} = h/e\,(\nu - \nu_0) - \mathrm{V}_0.$$

For the experiment to which fig. 14 refers, $\mathrm{V}_0 = -1{\cdot}07$, $\nu = 7{\cdot}40 \times 10^{14}$, and ν_0 is between $6{\cdot}02 \times 10^{14}$ and $6{\cdot}25 \times 10^{14}$. Consequently the contact potential K was between the two limits 1·544 and 1·639 volts. For the slightly different conditions ruling when the curves in fig. 12 were taken, the limits for the contact potential would be:—For the full curve with points thus, ⊙, 1·62 and 1·72 volts; for the series with points thus, ×, 1·78 and 1·88 volts.

§ 7.—*The Approach to the Voltage Axis.*

It is well known that photo-electric characteristic curves for monochromatic illumination approach the voltage axis at finite angles, indicating a finite limit to the maximum kinetic energy, whereas the characteristic curves for thermionic electron currents approach this axis asymptotically. An examination of figs. 4, 6, 7 and 12 suggests that in this respect the chemical electron curves differentiate themselves from the photo-electric and resemble the thermionic ones. The point is an important one for the interpretation of the results. It is, perhaps, not so easy to be sure about it as might appear from an inspection of the diagrams, inasmuch as in many cases this part of the curves depends on the measurement of small deflections liable to considerable errors. Probably the best way of testing this question is by photo-electric and chemical curves taken simultaneously, since any errors will then be liable to affect both curves in a similar manner. Fig. 15 shows the results of such an experiment with chlorine using the spherical electrode. The points marked × represent the relative chemical currents, and those marked ⊙ the relative photo-electric currents taken simultaneously. The values are relative to the − 3 volt values, and the currents were not saturated at this voltage. Some trouble arose during the measurements on the saturation part of the curve, and the value of the saturation current could not be got accurately, so that the vertical scale may be a little different from that of most of the other figures in this paper. This experiment leaves little doubt as to the reality of the gradual approach to the voltage axis in the case of the chemical effect. It is the more convincing because, during the determination of the two points at 0 and − 0·5 volts, the standard current at − 3 volts was increased to about 450 divisions per two minutes (cap. 0·01 mfd.); whereas, during the determination of the rest of the points in fig. 15, the standard current varied between 20 and 30 divisions per two minutes, with the same capacity. Notwithstanding this very great change in the absolute value of the standard current, the two end points are seen to fall on the same curve as the rest. The actual numerical values may be of interest and are given in the next table:—

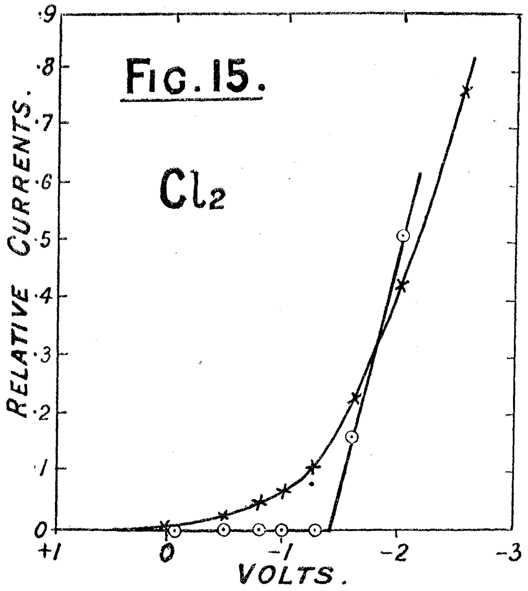


FIG. 15.

TABLE VII.—Chlorine.

Applied volts (voltmeter readings)	2·5	2·0	1·6	1·3	1·0	0·8	0·5	0
Chemical effect currents (scale divs. per 2 mins.)	18	11	6	3	2	1	8	2
Relative chemical currents	0·78	0·43	0·24	0·116	0·068	0·05	0·025	0·004
Relative photo-electric currents		0·51	0·16	0·00	0·00	0·00	0·00	0·00

The sensitiveness of the electrometer was 570 divisions per volt, the added capacity 0·01 mfd., making the total capacity equal to 0·01012 mfd.; the pressure was 0·002 mm. throughout and the pump running continuously in this experiment.

Fig. 16 shows some similar data for $COCl_2$, except that the photo-electric and chemical curves were not taken simultaneously. The photo-electric curves, with the mercury lines λ 4046 to λ 4077, were taken the day before the chemical data, and no doubt there was some alteration in the contact potential between the electrodes in the interval between the experiments. The chemical data shown by crosses are a replot of those similarly indicated in fig. 12. The photo-electric data, shown thus ⊙, are actual currents in scale divisions per minute, with a capacity of 0·01053 mfd. and an electrometer sensitiveness of 1100 divisions per volt. The saturation current was 130 in the same units in these photo-electric experiments. These curves again show quite clearly the reality of the small currents with relatively large opposing voltages for the chemical emission. The actual data for fig. 16 are shown on the next page.

The second, third and fourth rows in this table and the last but one refer to the chemical emission, the fifth, sixth and seventh and the last to the photo-electric. The corrections for the electrometer drift in the fourth and seventh rows have been reduced respectively to the same units as the corresponding deflections in the second and fifth. Assuming that the determinations are liable to errors of the same magnitude as this drift, an assumption which is certainly conservative, the small chemical current at + 0·12 volt should be reliable to within 30 per cent. and the errors in the others are comparatively trifling. The same test applied to the photo-electric data shows that the value at − 1·0 should be correct to 16 per cent., the value at − 0·4 meaningless and the others reliable. With regard to the small electrometer deflections recorded in some of these experiments, it should be pointed out that these can be measured with considerable confidence when the large capacities employed are added to the instrument. The pressure during these chemical measurements varied between the limits of 0·002 and 0·004 mm., and during the photo-electric between 0·0015 and 0·0025 mm.

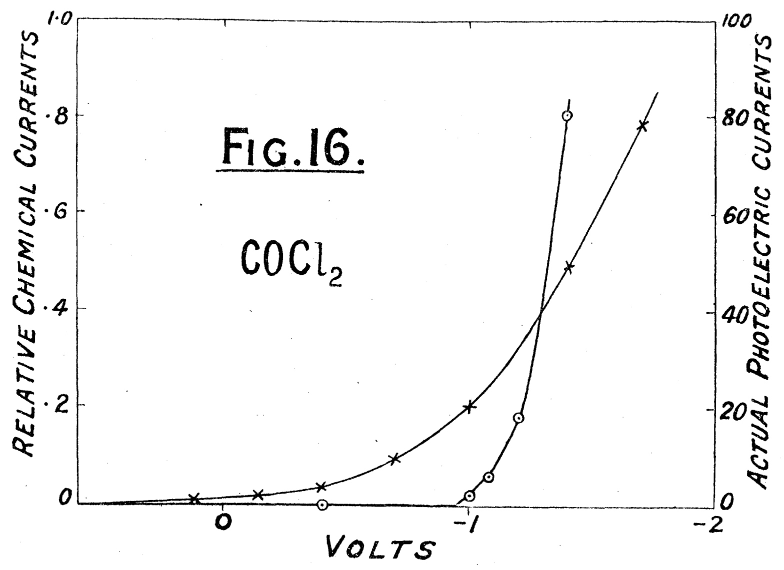


FIG. 16.

TABLE VIII.—$COCl_2$.

Applied volts (as given by voltmeter)	−1·7	−1·4	−1·2	−1·08	−1·0	−0·7	−0·4	−0·14	+0·12
Chemical current (scale divs./min.).	79	109			59	11	5	3	31
Capacity (mfd.)	0·02053	0·02053			0·02053	0·02053	0·02053	0·02053	0·00053
Correction for leak (scale divs./min.).	−0·26	−0·26			−0·26	−0·26	−0·26	−0·26	−10
Photo-electric currents (scale divs./min.).		80	360	114	34		−12		
Capacity (mfd.)		0·01053	0·00053	0·00053	0·00053		0·00053		
Correction for leak (scale divs./min.).		+0·35	+7	+7	+7		+7		
Relative chemical currents	0·785	0·490			0·200	0·092	0·034	0·016	0·0067
Photo-electric currents (scale divs./min. with cap. 0·01053)		80	18·5	6·08	2·06		−0·251		

On referring to fig. 12 it may be noticed that the values taken the following day and shown thus ⊙ on that diagram, are not in good agreement with the crosses on this part of the curve. However, they are nothing like so reliable. The reading at + 0·12 volt is only 15 per cent. of the electrometer drift; that at − 0·12, 37 per cent.; that at − 0·42, 80 per cent.; and it is not until the comparatively large relative current at − 1·0 volt is reached that the accuracy becomes better than that of the worst point shown in fig. 16.

§ 8.—*The Effect of the Different Gases on the Photo-electric Threshold Frequency.*

In the one case for which this frequency has been closely estimated ($COCl_2$) we have seen that it was very near to λ 4900 ($6 \cdot 02 \times 10^{14} < \nu_0 < 6 \cdot 25 \times 10^{14}$). This ν_0 is not to be regarded as a reliable constant, but one which varies with apparently trifling changes in the conditions. Thus in one $COCl_2$ experiment no photo-electric current could be got with the full light of the mercury lamp through the blue filter (mostly λ 4355). The chemical effect was working quite well and there was nothing otherwise to differentiate this experiment from others which gave quite large photo-electric currents with λ 4355. With this exception, so far as I can recollect or tell from the record, measurable photo-electric currents were always obtainable with λ 4355 both in $COCl_2$, chlorine and water vapour. With $COCl_2$ it is probable that the threshold frequency was always higher than that of the green line λ 5460 (frequency $5 \cdot 49 \times 10^{14}$). At any rate, tests made from time to time with the green filter never gave any deflections which could be relied on to mean anything. As regards chlorine, all that can be said is that the threshold frequency was less than that of λ 4355 ($6 \cdot 89 \times 10^{14}$) in all the experiments here referred to. In some of the tests with water vapour present it was found that not only λ 4355, but also the green line λ 5460 and the yellow line λ 5769 − λ 5790 gave photo-electric currents. The same was true of the light from a photographic dark-room lamp, and photo-electric currents were also obtained with the radiation from an incandescent lamp filtered through a solution of iodine in carbon disulphide of such strength as to make the lamp quite invisible through it. Evidently when water vapour is present the threshold frequency can lie in the infra-red part of the spectrum.

§ 9.—*Analysis of the Curves.*

The obvious way of attacking the problem of the distribution of kinetic energy among the emitted electrons is to take the curves, such as figs. 4, 7 and 12, and find the increments in current corresponding to equally spaced intervals dV along the voltage axis. These will be proportional to the number of electrons whose energies lie between eV and e (V + dV). This method will certainly give correctly, to the degree of accuracy within which it can be operated and to the accuracy within which V is known, the distribution of velocity among the electrons as they in fact reach the receiving electrode.

It is not so reliable a guide to the distribution among the electrons as emitted at the source, on account of the difficulty in estimating the effects of the factors enumerated on p. 11 *ante*, which tend to prevent the attainment of saturation at zero field, in modifying that distribution before the electrons reach the receiving electrode. The picture may also be distorted owing to the inexact location of the true zero of potential difference. A study of similar phenomena, as displayed by thermionically emitted electrons, supplies a useful guide towards the interpretation of the present chemical data. In the thermionic case it is found that such factors exert their major effect in distorting the original distribution in the neighbourhood of zero field, and the shapes of the curves in the larger retarding fields are little affected. Thus this method of analysis leads to much more reliable results for the faster than for the slower electrons.

Such an analysis, when applied to fig. 4, is shown in fig. 17, curve I.; when applied to fig. 7, in fig. 17, curve II., and when applied to fig. 12, in fig. 18. In each case an assumed zero has been taken which may be considerably wrong in the two curves in fig. 17, but which cannot be out by more than 0·10 volt in fig. 18, if, as I believe, the experimental determinations are reliable. Curves I. and II. of fig. 17 are seen to be very much alike and considerably different from fig. 18. The data in fig. 18 which are here referred to are the experimental points marked thus ⊙. The meaning of the crosses and the full curve on this diagram will be explained below. However, all three have certain important points in common. They show a distribution, such that for low energies the number within a given range $dE = edV$ varies only slowly with E

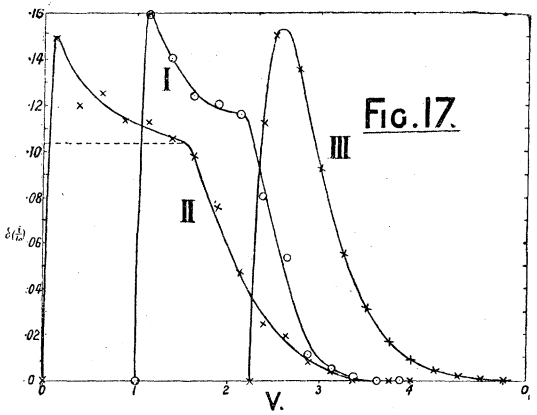


FIG. 17.

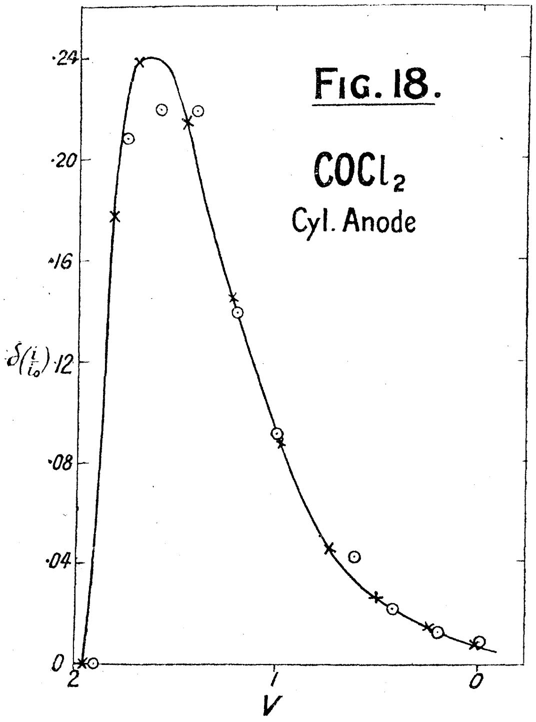


FIG. 18.

(or V), whereas for high energies, *i.e.*, further to the right on each diagram, it falls off very rapidly. Moreover, the shape of the rapidly falling part of the curve is much the same in each case, and in fact on this part of the curves the ordinates are very nearly proportional to $e^{-\alpha \mathrm{V}}$, where α is a constant for any one curve. This can be seen if the logarithms of the ordinates are plotted against V when the points fall very nearly on a straight line. On the other hand, the slowly varying part of the curve shows distinct indications of possessing a maximum in fig. 18, whereas in curves I. and II. it falls away continuously from the initial value. This disagreement at low energies suggests trouble from the factors referred to above and points to the desirability of keeping for the present to the high energy part of the curve in trying to find an interpretation of the results. The outstanding feature of this part of the curve is the fact that it falls away very approximately in proportion to the factor $e^{-\alpha \mathrm{V}}$, which at once suggests a Maxwell distribution of energy among the electrons, since this distribution is dominated by a factor of this form. I have therefore calculated the currents which would be obtained on the assumption that the energy of the electrons is a Maxwell distribution pertaining to some, as yet undetermined, temperature T, and compared the results of the calculations with the experimental data.

For a small source surrounded by a large electrode the direction of motion is immaterial, and it is only the magnitude of the total kinetic energy which determines whether the emitted electrons will reach the receiving electrode against a given retarding potential difference. If the distribution is Maxwellian, the proportion with energies between u and $u + du$ is equal to

$$\frac{\mathrm{A}}{k^2\mathrm{T}^2}\, u\, du e^{-\frac{u}{k\mathrm{T}}},$$

where A is an undetermined constant and k is Boltzmann's constant. They reach the surrounding electrode if $u \geqq e\mathrm{V}$. Hence the current against an opposing potential difference V is

$$i = \frac{\mathrm{A}}{k^2\mathrm{T}^2}\int_{e\mathrm{V}}^{\infty} u\, du e^{-\frac{u}{k\mathrm{T}}} = \mathbf{A}\left(1 + \frac{\epsilon \mathrm{V}}{k\mathrm{T}}\right) e^{-\frac{e\mathrm{V}}{k\mathrm{T}}}$$

$$= i_0\left(1 + \frac{e\mathrm{V}}{k\mathrm{T}}\right) e^{-\frac{e\mathrm{V}}{k\mathrm{T}}},$$

if i_0 is the value of i when $\mathrm{V} = 0$, *i.e.*, the value of the saturation current. If the currents are expressed as fractions of the saturation value, the proportion of the maximum current, or, what is equal to this, the proportion of the emitted electrons, having energies between the limits $e\mathrm{V}$ and $e(\mathrm{V} + d\mathrm{V})$, is given by

$$d\left(\frac{i}{i_0}\right) = \frac{e^2}{k^2\mathrm{T}^2}\, \mathrm{V}\, d\mathrm{V} e^{-\frac{e\mathrm{V}}{k\mathrm{T}}}.$$

The following table of values of these various quantities calculated, to the accuracy of the slide rule, for $\mathrm{T} = 1500°\mathrm{K}$, taking $e = 4 \cdot 8 \times 10^{-10}$ and $k = 1 \cdot 346 \times 10^{-16}$ will be found useful. These values happened to be computed for $T = 1500$ in connection with another matter. However, since all the functions are homogeneous in V/T, they can at once be applied to any other temperature T^1 by simply multiplying all the voltages by $T^1/1500$. Of course, in dealing with the values of $d\left(\frac{i}{i_0}\right)$ the appropriate value of the factor $\frac{e\,dV}{kT}$ has to be used. This can readily be ascertained for any values of T and dV from the numbers in the second column of the table.

Table IX.

V.	$\frac{eV}{kT}$.	$e^{-\frac{eV}{kT}}$.	$\left(1+\frac{eV}{kT}\right)e^{-\frac{eV}{kT}}$.	$\frac{eV}{kT}e^{-\frac{eV}{kT}}$.
0	0	1	1	0
0·05	0·398	0·672		0·268
0·10	0·795	0·452	0·809	0·360
0·20	1·59	0·205	0·528	0·326
0·30	2·385	0·0926	0·314	0·222
0·40	3·18	0·0418	0·175	0·133
0·50	3·975	0·0189	0·0940	0·0751
0·60	4·77	0·00855	0·0493	0·0408
0·70	5·565	0·00386	0·0253	0·0214
0·80	6·36	0·00175	0·0129	0·0111
0·90	7·155	0·000787	0·00642	0·00563
1·00	7·95	0·000355	0·00318	0·00282
1·10	8·745	0·000160	0·00156	0·00140
1·20	9·54	0·0000730	0·000768	0·00070
1·30	10·335	0·0000331	0·000374	0·00034
1·40	11·13	0·0000148	0·000179	
1·50	11·925	0·0000068	0·000088	

A set of values of $\frac{eV}{kT}e^{-\frac{eV}{kT}}$ is plotted, on an arbitrary scale, in curve III., fig. 17. The right-hand part of this shows a close resemblance with the rapidly dropping parts on the right-hand sides of curves I. and II., but the low-voltage parts of the curves are quite different. Apart from the difference in shape, the low-voltage parts of I. and II. are much broader than in the case of III. relative to the rest of the figure. However, the breadth here is determined entirely by the assumed position of the zero. In curve II. this is at 1 volt in fig. 17 and corresponds to the zero in fig. 4. This zero has, however, been shown to be at least 0·12 volt outside the possible limits for the true zero as determined by the photo-electric data, and it may quite well be out by as much as half a volt. In that case curve I. would have to come up from the volt axis at about 1·5 volts instead of at 1 volt, which would have made the curve show a much stronger resemblance to curve III. The position of the true zero for the chlorine data plotted in curve II. is still more doubtful. These curves illustrate well the difficulties involved in the analysis of the energy distribution unless the position of the zero is correctly known.

In fig. 18, which refers to the data for $COCl_2$ with the cylindrical electrode, the position of the actual zero is known to within 0·10 volt, and it is obvious that these experimental points (marked thus ⊙) show a much closer resemblance to the requirements of the Maxwell distribution. The crosses in this figure do, in fact, represent a Maxwell distribution for the temperature $T = 3600°K$, and the same range $dV = 0·20$ volt as the experimental points deduced from fig. 12, and the full curve is drawn to meet the theoretical points. It will be seen that the points given by the experiments are very close to the theoretical curve, and, in fact, the agreement is as close as could be expected, except in the immediate neighbourhood of the maximum. As has been explained already, there are disturbing causes which are likely to produce deviations in this region, and these deviations should be in the direction indicated by the discrepancy shown by the diagram. It should be pointed out that the only quantity which can be arbitrarily varied in fitting the theoretical curve to the experimental points is the single parameter T. The only other variable entering is the stretch dV, which is already fixed by the way in which the experimental points are reduced from the observational data. Given T and dV, the value of the ordinate for any particular value of V is determined absolutely.

I believe that the data exhibited in fig. 18 furnish strong evidence that the distribution of energy among the chemically emitted electrons is of a very simple character and is identical with that which would be possessed by the molecules of a gas at a certain definite temperature. The fraction where kinetic energy lies between u and $u + du$ appears, in fact, to be given by

$$\frac{dn}{n} = \frac{du}{kT}\,\frac{u}{kT}\,e^{-\frac{u}{kT}}.$$

For $COCl_2$ acting on NaK_2 the value of T appears to be close to 3600° K. The evidence would, of course, be stronger if it were unequivocally supported by the analysis of figs. 4 and 7. It may be that too much emphasis is being laid on the uncertain data and the disturbing causes which affect curves I. and II. of fig. 17. It may be that there is something real in the extra width of the low-voltage parts of the curves. Something of this kind might arise on the not improbable contingency that, in reality, more than one temperature T is involved. It is impossible to give a definite answer to such questions until more experimental evidence is forthcoming, but another basis of judgment on the data now available may be got by treating them a little differently.

Instead of dealing with the proportion of electrons whose energies lie between eV and $e(V + dV)$, I shall now calculate the fraction of the saturation current which will be able to flow against an opposing potential V on the assumption that the initial velocity distribution is a Maxwell distribution for some temperature T, and compare the result with the experimental characteristic curves. The values of such currents for $T = 1500$ are the values of $\left(1 + \frac{eV}{kT}\right) e^{-\frac{eV}{kT}}$ in the fourth column of Table IX. for the voltages in the same row given by the first column. For any other value T^1 of T the corresponding voltages are obtained by multiplying the values in the first column by the ratio $\frac{T^1}{1500}$. In determining the appropriate value of T the values of i/i_0 have been made to fit the experimental characteristics at 0·314 and at 0·0493. Unless the position of the zero on the voltage scale is known, it is necessary to fix two points in this way in order to determine the scale of T. Once this is done, all the other points are given by the corresponding numbers in the fourth and first columns of Table IX., subject to the transformation of the voltages in the first column in the ratio of the temperatures. Incidentally it may be remarked that this process, subject to the correctness of the hypothesis, gives the true zero as the point at which the value of i/i_0 becomes unity. This affords a further check on the interpretation of the data. The results of this treatment are shown in figs. 19, 20 and 21, which will now be considered in turn.

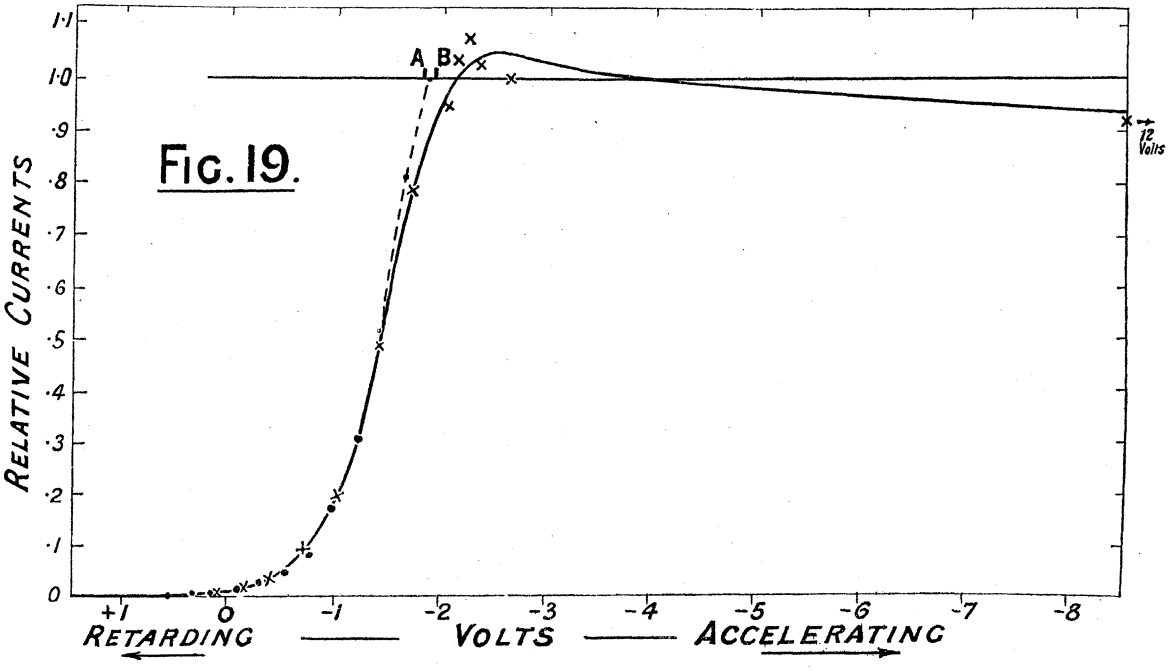
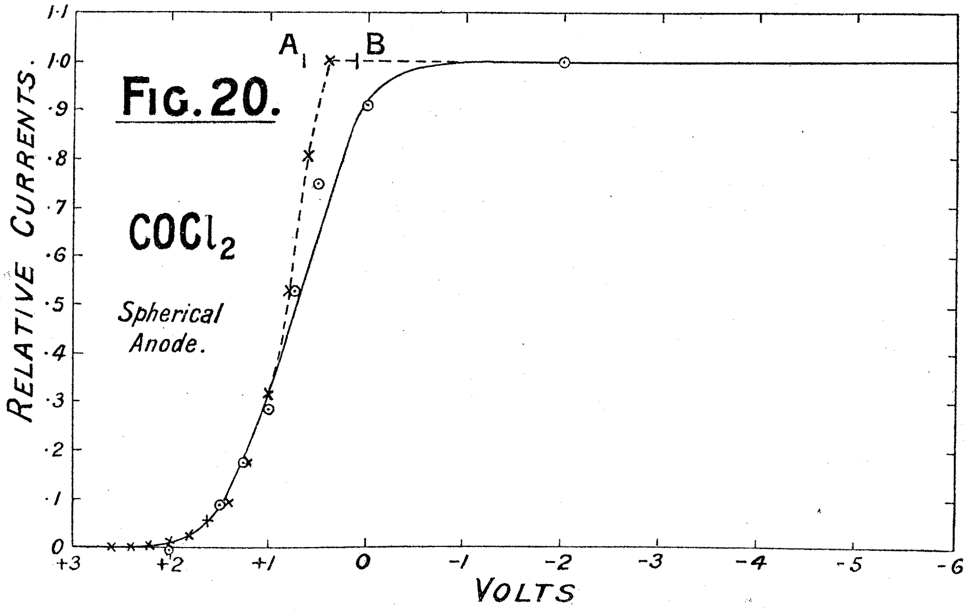


FIG. 19.

The full curve in fig. 19 is a replica of fig. 12, and the crosses denote the series of experimental points on which it is based. The auxiliary series of points in fig. 12 have been left out for clearness. The currents calculated as explained are shown by the points marked thus •, and when necessary the curve joining them is indicated by a broken line. This line, therefore, gives the characteristic as it would be if it were determined entirely by the distribution of velocity of the electrons, and if this were a Maxwell distribution for the temperature T = 3300°K, which is the value given by fitting the points referred to above. It will be seen that the theoretical curve agrees with the experimental characteristic for all retarding voltages exceeding about $-0\cdot20$ volts. There is a small deviation in the neighbourhood of zero volts which is the counterpart of the discrepancy between the theoretical curve and the experimentally derived points in fig. 18 in the same region. This process places the true zero voltage at $-1\cdot84$ volts in figs. 12 and 19; the limits assigned by the photo-electric measurements were $-1\cdot78$ and $-1\cdot88$ volts, and the value here found lies almost midway between them.

Fig. 20 deals similarly with the earlier data for $COCl_2$ given by the spherical electrode. The full curve is the composite curve of fig. 4 and the points ⊙ denote the best single



set of data on which this curve is based. The crosses denote the calculated values on the assumption of MAXWELL'S distribution, the fit at the two assigned points requiring a value of T = 3000 in this case. The broken lines show the theoretical characteristic as thus calculated. It will be seen that the agreement with the composite curve is satisfactory at the higher retarding voltages (shown on the left of the diagram), but that the deviation in the neighbourhood of zero volts is much more considerable than in fig. 19. However, this deviation is greatly minimised if the circular points are considered rather than the composite curve, and it may be that the rather considerable errors in the determination of this part of the curve have displaced it unduly to the right-hand side. In any event the deviation is of such character and magnitude that further investigation may assign it to causes outside the energy distribution. The true position of zero volts given by this calculation is + 0·40 volts on the scale and is well within the limits, marked by vertical lines at A and B on the diagram, set by the photo-electric observations.

It will be seen that figs. 18, 19 and 20 lead to three separate estimates of the value of T for the case of $COCl_2$, viz., 3600, 3300 and 3000. Of these the first and second use the same experimental data but treat them in different ways. The third employs different data but treats them in the same way as the second. The mean of these determinations is T = 3300°K. It is probable that an agreement to within 10 per cent. of the value of T is as much as it is reasonable to expect at the present stage of development of the subject.

Turning to fig. 21, the full curve is a copy of the chlorine curve in fig. 7 and the broken curve represents the theoretical characteristic assuming a Maxwell distribution, the calculated points being shown by the crosses. The value of T for this curve was found to be 4350. The general appearance of fig. 21 is the same as that presented by the $COCl_2$ data in fig. 20, and, in general, the same remarks apply to both curves. The triangular area CDE, which measures the discrepancy between the calculated curve and the experimental characteristic, is somewhat larger in fig. 21 than in fig. 20, but the increase is only about in proportion to the greater horizontal extension of the chlorine diagram corresponding to the higher value of T. Whatever the difference between the full and broken curves is due to, it is probably caused by similar factors operating in the case of both gases. The value of the true zero given by the calculated curve in fig. 21 is −3·11 volts, which is well to the right of the left-hand limit −2·17 volts

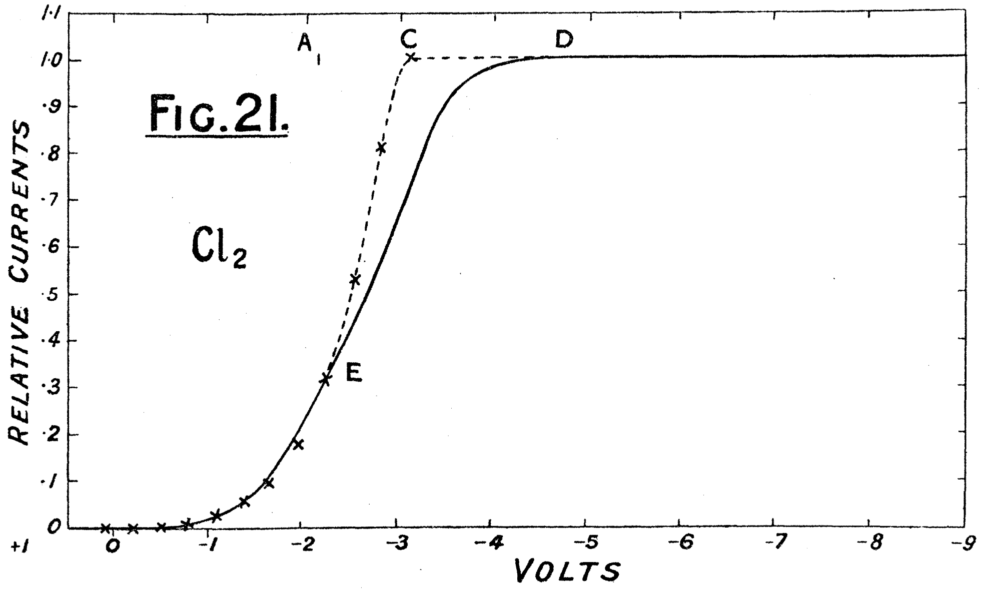


FIG. 21.

set by the photo-electric currents and shown at A. The right-hand limit could not be determined at this stage.

Another estimate of the value of T for chlorine can be got by assuming that for $COCl_2$ and comparing the widths of corresponding parts of curves such as I. and II. in fig. 17. Keeping to the rapidly falling parts of these curves, which are comparatively free from errors due to the uncertain zero and to the disturbing causes in its neighbourhood, I find that the width from the $66\frac{2}{3}$ per cent. point to the 4 per cent. point, is for chlorine, 1·387 volts, and for $COCl_2$, 0·840 volt. Taking the value of T for $COCl_2$ to be 3300, this would give the value for chlorine as $3300 \times \frac{1\cdot387}{0\cdot840} = 5450$. This is considerably higher than the value got from a study of fig. 21, but it will be remembered that the corresponding operation on fig. 20 also gave a low value for $COCl_2$. Under the circumstances probably the best estimate that we can make for chlorine is the mean of the two values, viz., 4900°K.

In each case the position of the true zero given by assuming the Maxwell distribution falls within the limits set by the direct photo-electric measurements. If we assume that the position of this zero is correctly fixed in this way, we can get another check on the relative values of T. The displacement in volts from the zero to the place where the current is a fixed small fraction of the saturation value, small enough to avoid the disturbances in the neighbourhood of zero volts, should be in the proportion of the respective values of T. The three sets of data give the following results, using 0·05 as the value of the small fraction :—

$COCl_2$ *Cylindrical anode*—

$$\left.\begin{array}{lcl}\text{zero} \;\; . \;\; . \;\; . \;\; . & = & 1\cdot84 \\ \text{5 per cent.} \;\; . \;\; . & = & 0\cdot52\end{array}\right\}\text{Displacement} = 1\cdot32 \text{ volts.}$$

$COCl_2$ *Spherical anode*—

$$\left.\begin{array}{lcl}\text{zero} \;\; . \;\; . \;\; . \;\; . & = & 0\cdot40 \\ \text{5 per cent.} \;\; . \;\; . & = & 1\cdot60\end{array}\right\}\text{Displacement} = 1\cdot20 \text{ volts.}$$

Cl_2 *Spherical anode*—

$$\left.\begin{array}{lcl}\text{zero} \;\; . \;\; . \;\; . \;\; . & = & 3\cdot11 \\ \text{5 per cent.} \;\; . \;\; . & = & 1\cdot36\end{array}\right\}\text{Displacement} = 1\cdot75 \text{ volts.}$$

The numbers 1·32, 1·20 and 1·75 are in the proportion 3300, 3000 and 4400, and are therefore in agreement with the values already obtained.

§ 10.—*Thermo-chemical Considerations.*

An upper limit to the value of T can be obtained from thermo-chemical data. From Recueil de Constantes Physiques,’ pp. 333 and 339, it appears that the heats of certain relevant chemical reactions are as follows :—

$$2K + Cl_2 \longrightarrow 2KCl + 208 \cdot 1 \times 10^3 \text{ gm. cals.}$$

$$2Na + Cl_2 \longrightarrow 2NaCl + 197 \times 10^3 \text{ gm. cals.}$$

$$2C + O_2 + 2Cl_2 \longrightarrow 2COCl_2 + 88 \cdot 2 \times 10^3 \text{ gm. cals.}$$

$$2C + O_2 \longrightarrow 2CO + 52 \cdot 2 \times 10^3 \text{ gm. cals.}$$

The data are for solid K, Na, KCl and NaCl, for carbon in the form of diamond, and for gaseous Cl_2, O_2, CO and $COCl_2$, in each case per gramme molecule, with the equations as written. It is difficult to conceive of any way in which the average energy of the electrons could exceed the equivalent of the heat of formation of two molecules of KCl from two molecules of K and one of Cl_2; in fact, it is practically certain to be much less than this. In general, if H is the heat available in gm. cals. per gramme molecule we shall have as a limit for T

$$\tfrac{3}{2}k\mathrm{T} \leqq \frac{\mathrm{JH}}{\mathrm{N}},$$

where k is Boltzmann's constant $1 \cdot 346 \times 10^{-16}$, J is the mechanical equivalent of heat $4 \cdot 184 \times 10^7$, and N is the number of molecules per gramme molecule $6 \cdot 2 \times 10^{23}$. If we put $\mathrm{H} = 208 \cdot 1 \times 10^3$ this gives as a limit for T the value $69 \cdot 7 \times 10^3$. This is about 14 times the value deduced from the experiments. However, something has to be subtracted from the value of H for the unknown heat of formation of the liquid alloy from the solid constituents, and the assumption that the whole heat of the reaction is passed on to one electron is only worthy of consideration for the purpose of fixing a limit for T. It is much more likely that the heat available is evenly divided among the different atoms taking part in the reaction. The number of these is doubtful owing to the somewhat uncertain degree of association of the reacting atom with its neighbours in the alloy. It is also possible that the actual reaction in which an electron is expelled is not correctly expressed by the equation of the end products written above, but is some intermediate reaction, such as

$$K + Cl_2 \longrightarrow KCl + Cl$$

or

$$NaK_2 + Cl_2 \longrightarrow NaK + KCl + Cl,$$

or the like. In such a case the value of the heat available may be quite different from that given by the end products. It is impossible to make any precise statements where the data are so indefinite, but I feel that when all these factors are taken into account the value of T given by the experiments on chlorine is a reasonable one.

This position is strongly supported when the value given by $COCl_2$ is compared with that given by Cl_2. It is most likely that the mechanism of the reaction is much the same in both cases, any difference arising mainly from the fact that the Cl_2 is now loaded up with the CO group. This would have two effects. It would reduce the total amount of energy available by the difference of the heats of formation of CO and $COCl_2$, *i.e.*, by 18×10^3 gm. cals. for each gramme molecule of $COCl_2$, and it would increase by two the number of atoms among which the energy is divisible. Let us consider a supposititious case in order to see what the effect of these differences will be. If we assume 6 as a reasonable number of atoms, including electrons as a special kind of atom, to be concerned in the reaction which emits an electron in the case of chlorine, there will be two more, or eight, in the case of $COCl_2$. Six atoms in the case of Cl_2 require a value of $H = 88 \cdot 4 \times 10^3$ to give $T = 4900$. This value of H is about half the total given by the equation of the end products after making a probable allowance for the unknown heat of formation of the liquid alloy, and is thus not unreasonable if the reaction in which the electron is emitted is of an intermediate type. The value of H for the case of $COCl_2$ now becomes $88 \cdot 4 - 18 = 70 \cdot 4$, and one-eighth of this is $8 \cdot 8$, which on division by $\frac{2}{3} \frac{J}{kN}$ gives $T = 2950$, a value quite near to that given by the experiments. This argument shows that the values of T deduced from the experiments are not in conflict with thermo-chemical data so far as our knowledge of the reactions enables us to apply it.

In conclusion I wish to thank my assistant, Mr. J. W. Burrows, for his invaluable help. I also gladly acknowledge my indebtedness to the Government Grant Committee of the Royal Society for a grant which has defrayed part of the cost of the apparatus and materials used.