

V. On the determination of chemical affinity in terms of electromotive force—Part VII

C.R. Alder Wright D.Sc. F.R.S. & C. Thompson

To cite this article: C.R. Alder Wright D.Sc. F.R.S. & C. Thompson (1883) V. On the determination of chemical affinity in terms of electromotive force—Part VII, Philosophical Magazine Series 5, 16:97, 25-48, DOI: [10.1080/14786448308627390](https://doi.org/10.1080/14786448308627390)

To link to this article: <http://dx.doi.org/10.1080/14786448308627390>



Published online: 28 Apr 2009.



Submit your article to this journal [↗](#)



Article views: 4



View related articles [↗](#)

same clearness of tone which distinguishes the same arrangement in air at the ordinary pressure from that in a vacuum. The degree of vacuum existing in the bulbs is that of the usual incandescence lamp, or about one millionth of an atmosphere.

It might be thought from M. Edlund's researches, recently referred to in the *Philosophical Magazine*, that polarization of the metal contacts would prevent the microphonic action *in vacuo*; but this is evidently not the case.

V. *On the Determination of Chemical Affinity in terms of Electromotive Force.*—Part VII. By C. R. ALDER WRIGHT, D.Sc. (Lond.), F.R.S., Lecturer on Chemistry and Physics, and C. THOMPSON, Demonstrator of Chemistry, in St. Mary's Hospital Medical School*.

On the Electromotive Force of Clark's Mercurous-Sulphate Cell; and on the Work done during Electrolysis.

On the E.M.F. of Clark's Cell.

133. **I**N the course of the series of experiments partly described in Parts V. and VI. a large number of observations have been made with various cells after Clark's construction (*Proc. Roy. Soc.* xx. p. 444), in all cases compared with one another and with other cells by means of the quadrant-electrometer only, so that they never generated any current other than the minute leakage current through the not mathematically absolutely insulating materials between their poles.

In some instances the mercurous sulphate was purchased (from Messrs. Hopkin and Williams), and was well washed before use by numerous boilings with distilled water and decantations. In other cases the mercurous sulphate was prepared by heating twice-distilled mercury (previously purified by nitric acid) with pure sulphuric acid at as low a temperature as possible consistent with any action taking place, and thoroughly washing the resulting sulphate by repeatedly boiling with distilled water and decantation. The action was never allowed to go on until more than a fraction of the mercury used was converted into sulphate, in order to reduce the amount of mercuric sulphate formed to a minimum.

The cells were made out of pieces of ordinary combustion-tubing (selected on account of the absence of lead in the glass)

* Communicated by the Physical Society, having been read May 12, 1883.

drawn out before the blowpipe into the U-shape represented on about two thirds scale in the cut (fig. 1). The glass being perfectly dry and hot, pure recently-boiled still hot mercury was poured into them so as to form a layer about half an inch (10 to 15 millimetres) deep, *a*; on the top of this was then poured a boiling paste of thoroughly well-washed mercurous-sulphate and zinc-sulphate solution, containing so much of the latter salt as to be slightly supersaturated when cold, so as to crystallize on standing. It was found convenient to make the paste not too thick, and to let the solid matter subside in the cell, the supernatant comparatively clear fluid being sucked out by a clean pipette, so as finally to leave on the top of the mercury a layer of particles of mercurous sulphate wetted with zinc-sulphate solution some 15 to 20 millimetres deep, *b*. Pieces of zinc rod (cast in glass tubes from pure metal fused in a porcelain crucible), well brightened by a file that had never touched any other metal, were then placed in the cells so as to dip into the paste some 4 or 5 millimetres, and project out of it about twice as much, *c*. The zincs were kept from falling by pieces of cork, *d*, cut as represented in fig. 2, and previously immersed in hot paraffin-wax so as to expel air and moisture; to the ends projecting from the paste were previously soldered copper wires, *e*. Melted paraffin-wax was then poured into the cell so that all air was expelled, rising through the perforations in the edges of the cork disks, and so that the upper two thirds of the zinc and the soldering were completely covered, *f*. Finally, a piece of platinum wire, *g*, or a strip of foil was passed down the narrow limb of the cell so as to make contact with the mercury: it was found convenient to amalgamate the tip of the platinum by moistening it and immersing it in freshly made sodium amalgam, all sodium being removed from the adherent film of mercury by subsequent immersion in water for some hours. The cells thus prepared, being wanted for use only and not being required to be externally well finished, were not mounted in the neat brass cases with ebonite tops and binding-screws usually employed, but were simply fixed in a beaker, or any other convenient holder, by pouring in melted paraffin-wax around them. When used in connexion with the electrometer, the copper wire soldered to the zinc and a similar wire soldered

Fig. 1.

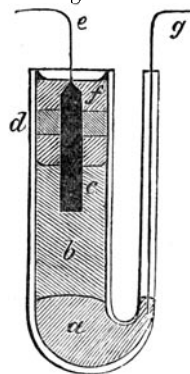


Fig. 2.



to the strip of platinum (and secured by a turn round the upper end of the narrow limb and a drop of sealing-wax) were bent over so as to dip into mercury-cups, a number of which were arranged in the arc of a circle round two others, like those figured in Part V.; so that any consecutive pair of cups could at will be connected with the electrometer by the double switch.

Either through a natural repulsion between bright zinc and the mercurous-sulphate paste, or through the formation of a faint film of grease &c. on the zinc from the file used to brighten it, it sometimes happened that the cell when finished would not work, contact not existing between the zinc and paste. It was found that this never occurred when the brightened zincs were washed successively with ether, alcohol, and saturated zinc-sulphate solution just before immersion in the paste.

134. On comparing together a moderately large number of cells (upwards of fifty) thus prepared with different specimens of mercurous sulphate, readings being taken two or three times a week for some three months, the following results were obtained:—A slight rise in E.M.F. was often observed during the first few days after construction; but at the end of a week at most the values *became constant, and remained so (the temperature being constant) for long periods of time.* The maximum variations observed between the average results of the series of observations for any two given cells were slightly less than that found to exist by Clark (whose highest and lowest values are respectively 1·4651 and 1·4517 volt, giving a difference of 0·0134 volt, or upwards of 0·9 per cent.). Taking the average of the whole set as 100·00, the maximum variation between two single cells did not exceed 0·10 volt, or 0·7 per cent., each cell possessing a value lying between 99·65 and 100·35. Even amongst cells set up at the same time from absolutely the same materials, extreme differences of as much as 0·005 volt = 0·35 per cent. were sometimes observed, although usually the difference did not exceed 0·002 or 0·003 volt and was frequently almost inappreciable.

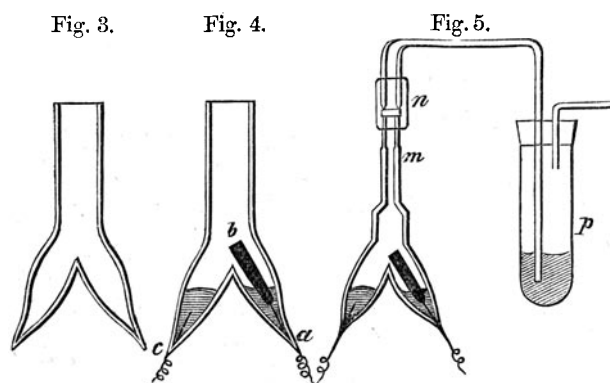
Much greater differences, however, were found to exist when the zinc-sulphate solution was not completely saturated with that salt, the variation produced being of this kind, that *the weaker the solution the higher the E.M.F. of the cell*, the difference being approximately proportionate to the amount of dilution, and amounting to upwards of 2·0 per cent. of the value when considerably dilute zinc-sulphate solution was used. The details of these observations will be discussed in a future paper, along with those of similar experiments made

with other cells. It may, however, be here noticed that, so long as a cell containing unsaturated zinc-sulphate solution was protected against concentration by evaporation, and was only used in connexion with a quadrant-electrometer, its indications remained perfectly constant for many months (the temperature being the same), precisely as was found with cells set up with saturated zinc-sulphate solution.

Effect of Dissolved Air on the E.M.F. of Clark's Cell.

135. Two series of experiments were made with the object of finding out how far the boiling of the mercurous-sulphate paste (as recommended by Clark) in order to remove dissolved air is essential. In one series a number of cells were set up, using fully aerated zinc-sulphate solution and unboiled mercury (exposed to the air under a glass shade for several days since preparation and distillation respectively); in the other the paste was boiled in a Sprengel vacuum produced in the cell itself for some time, the cell being then hermetically sealed, so as to reduce the amount of residual air to a minimum. In each case the average E.M.F. of the combination was *sensibly identical with that of an average ordinary Clark cell* prepared as above described and containing zinc-sulphate solution of the same strength as that contained in the combination.

In order to prepare these hermetically-sealed cells a rather troublesome process was employed. First a piece of glass tubing, about 10 or 12 millim. in bore, was blown into a Y-shape, and the two limbs of the Y drawn out as represented in fig. 3; a zinc rod was then cast so that a thin platinum wire was imbedded in one end; this zinc rod was brightened and



sealed up on the tube so that the platinum wire projected (fig. 4, *a*). By the aid of a glass funnel with a flexible capil-

lary stem (made by drawing out a piece of tubing before the blowpipe) paraffin-wax was introduced into the sealed-up limb so as to cover up completely the platinum wire and lower half of the zinc, leaving the other half exposed, *b*. In a similar way, recently boiled mercury was run into the other limb, previously sealed up with a second platinum wire passing through the glass, *c*. The stem of the inverted Y-tube was then carefully drawn out before the blowpipe (fig. 5, *m*), and connected by means of a short piece of india-rubber tubing, *n*, with the end of a glass tube projecting from the little flask, *p*, containing mercurous sulphate paste, and connected with the Sprengel pump. When a fairly good vacuum was obtained, the paste was made to boil by applying a very gentle heat; after about half an hour's boiling (the pump being at work the whole time) the connexion between the pump and flask was suddenly severed, when the sudden access of atmospheric pressure drove the paste into the cell, completely filling it: the pump was then again connected, and the boiling carried out again in the cell itself, and so on as before. Finally, by means of a blowpipe the drawn-out stem was sealed at *m*. To prevent the paste blocking up this drawn-out part, it was found necessary to use levigated particles of mercurous sulphate with a large proportion of zinc-sulphate solution; so that ultimately the cell contained much more fluid than solid matter. In order to use the cell, copper wires were soldered to the platinum wires projecting from the sealed ends of the inverted Y and bent over so as to dip into mercury-cups, the Y being either held by a clamp or imbedded in paraffin-wax, and of course being never allowed to be upset or shaken up so that the mercury could pass into the limb containing the zinc, which is otherwise liable to occur and spoil the cell.

136. The following numbers may be quoted as illustrations of the practical absence of any effect on the E.M.F. of the cell caused by the presence or otherwise of dissolved air. The values cited are the average readings, during a period of several months, of a dozen cells set up with cold-saturated zinc-sulphate solution well aerated, and *not* sealed up with melted paraffin-wax, but only loosely corked to avoid entrance of dust. Each cell during this period remained sensibly constant. All the values are reduced to the average reading (taken as 100.00), during the same period, of a yet larger number of cells prepared hot and sealed up precisely in accordance with Clark's directions—this average reading being the standard employed in the previous portions of these experiments, and especially in Parts V. and VI.

Batch of four cells made from mercurous sulphate purchased from Messrs. Hopkin and Williams	{	No. 1.	99·90
		” 2.	99·94
		” 3.	99·95
		” 4.	99·99
Batch of four cell made from mercurous sulphate prepared specially by ourselves for this purpose	{	” 5.	99·75
		” 6.	99·95
		” 7.	99·99
		” 8.	100·02
Batch of four cells made from another specimen of mercurous sulphate prepared by ourselves	{	” 9.	99·97
		” 10.	100·11
		” 11.	100·18
		” 12.	100·19
General average			99·995

Precisely analogous figures were obtained with several vacuum-prepared cells, no one of which gave a value outside of the limits 99·7 and 100·3, *i. e.* outside of the limits of fluctuation of the ordinary Clark's cells compared with them. On opening one of these vacuum-cells so as to admit air, a distinct fall in E.M.F., amounting to 0·25 volt, was observed; this behaviour, however, was not shown by other similar cells on opening.

Influence of Mercuric Sulphate in the Mercurous Sulphate.

137. However carefully the mercurous sulphate may be prepared, it is almost impossible to obtain it without some admixture of mercuric sulphate. During the boiling and washing by decantation this latter becomes a basic salt, the so-called “turpeth mineral,” which possesses a bright yellow tint, and communicates to the mercurous sulphate a more or less pronounced yellowish tinge. In order to see how far the presence of varying quantities of this compound might possibly affect the E.M.F. of Clark's cell, several cells were set up in the same way as the hot-prepared cells described above, but using turpeth mineral only instead of mercurous sulphate. Two samples of turpeth mineral were employed:—one purchased (from Messrs. Hopkin and Williams), and well washed by boiling up many times with water and decantation before use; the other prepared by boiling mercury with a large excess of pure sulphuric acid, evaporating off most of the acid (which process converts all mercurous sulphate present into mercuric), adding to a large bulk of boiling water and washing many times the yellow heavy powder formed, by boiling up with water and decanting, so as to remove all traces of free sulphuric acid, and of the soluble acid mercuric sulphate also

formed. On taking a long series of readings of these cells, it was found that whilst the E.M.F. was, when the cell was newly set up, close to that of an average mercurous-sulphate cell, on standing a few days a distinct fall was observable, which went on progressively until, after some weeks, a diminution in the E.M.F. of between 3 and 4 per cent. was brought about, after which the fall ceased or became very languid. Thus the following average readings were obtained as before, the average E.M.F. of the hot-prepared cells containing saturated zinc-sulphate solution being taken as 100 when at the same temperature as the cells examined: cells A, B, C, and D were set up simultaneously with turpeth mineral prepared by ourselves; cells E and F simultaneously with the purchased substance. The zinc, zinc sulphate, and mercury used were the same as those used for the hot-prepared cells. Notwithstanding, however, that all the cells were as alike as possible, yet the rate of fall during the first few weeks was by no means identical.

Age of cell...	1 day.	2 to 6 days.	1 to 2 weeks.	6 weeks.	2 to 4 months.	6 to 20 months.
Cell A	100·6	100·12	99·95	98·35	97·04	97·00
„ B	100·3	100·31	100·11	99·65	98·18	97·64
„ C	100·4	100·22	99·90	99·19	97·38	96·96
„ D	100·6	100·46	99·80	97·88	97·39	97·44
Average	100·5	100·28	99·93	98·77	97·50	97·26
Cell E	99·4	98·85	97·27	96·78	95·80
„ F	99·5	99·41	98·13	97·11	96·00
Average	99·45	99·13	97·70	96·95	95·90

It is evident from these figures that the effect of the presence of turpeth mineral in the mercurous sulphate used for Clark's cells is in the direction of decreasing the value; but inasmuch as the decrease is progressive, whilst no such alteration was observed in the Clark's cells examined, at any rate during several months after construction, it appears doubtful whether the variations in the E.M.F. of different Clark's cells set up at various times can be attributed to this cause.

Permanence of Clark's Cells.

138. A number of cells prepared in various ways (paste boiled and cells sealed with paraffin-wax; paste boiled *in vacuo* and cells hermetically sealed; set up with saturated zinc-sulphate solution, or with weaker solutions) were kept for periods of time ranging from a few months to two or three years, and

checked against one another from time to time, or compared with Daniell cells set up as described in Part V., with amalgamated pure zinc and electro-copper plates, and pure zinc- and copper-sulphate solutions of the same molecular strength*. No permanent changes in the values were observed (outside of the limit of the errors of observation) in the case of those cells which were so well sealed that neither evaporation took place, nor passage outwards of the fluid by capillary action through cracks in the sealing material. Vacuum-cells were thus kept unchanged for upwards of two years, as also were some normal Clark cells that were completely imbedded in paraffin-wax. In several cases, however, where the cells were not completely imbedded, but were only sealed up by a plug of paraffin-wax poured in at first round the zinc plate and the cork &c. supporting it, cracks formed sooner or later either in the paraffin-wax itself or between the glass and the wax, so that the fluid passed out through the cracks by capillary action and formed an efflorescence outside the cell. In some cases the action went on to such an extent as to leave the zinc wholly exposed, no contact finally existing between it and the paste: such cells were of course utterly spoilt. In other instances the zinc was only partially bared: in these cases the E.M.F. of the cell remained almost unaltered when saturated zinc-sulphate solution was employed in the first instance, but was lessened when unsaturated solution was originally used, owing to the evaporation and concentration which went on simultaneously with the capillary action, or subsequently to the commencement thereof. For example, two cells set up

* A large number of observations on the E.M.F. of Daniell cells have shown that, when proper precautions are taken in setting up the cells, a very considerable degree of constancy in value is attainable, so that such cells serve as good practical standards; but that if these precautions are neglected, *variations amounting to 5 per cent., and even more, may ensue.* The essential precautions are:—first, that pure solutions of zinc and copper sulphates containing no free acid should be used, each being of the same molecular strength (*i. e.* practically of the same specific gravity; conveniently the molecular strength may be near to MSO_4 , $50\text{H}_2\text{O}$); secondly, that the solutions should be in separate vessels, united when required by an inverted U-tube, the mouths of which are covered with thin bladder (Raoult's form of cell); thirdly, that the plates should be pure zinc amalgamated with pure mercury, and copper recently electro-deposited from pure sulphate solution—the wires serving as electrodes, and their junctions with the plates being coated with gutta-percha, so that no part of the plate or wire is simultaneously in contact with both fluid and atmosphere; and fourthly, that, if used to generate a current, the current-density must not exceed some 5 microamperes per square centimetre, so that with plates exposing 20 square centimetres the total resistance in circuit must be *at least* 10,000 ohms, if exposing 10 square centimetres 20,000 ohms, and so on.

with zinc-sulphate solution about two thirds saturated gave the values 101·07 and 100·92 during the first few weeks after construction; cracks then formed, and efflorescence and evaporation took place, so that the zincs became partially bared, during which time the electromotive forces gradually sank. After some months the paste became covered with crystals of zinc sulphate, indicating that the residual solution moistening the mercurous sulphate was saturated: the electromotive forces were then 100·13 and 99·73 respectively, which values were subsequently retained almost constant for several months longer, notwithstanding that a considerable portion of each zinc rod was out of the paste and exposed to the air.

A number of observations made with cells containing zinc rods partly immersed in the paste and partly exposed to the air, gave sensibly the same average result as another series of observations made with the same cells when the zinc rods were pushed down so as to be wholly immersed (the upper end and the wire serving as electrode being protected from contact with the paste by gutta-percha).

It is specially to be noticed, in connexion with the question of the permanence of Clark's cells, that the cells experimented with were only used in connexion with the quadrant-electrometer; so that from first to last they *never generated any continuous current, nor had any current (however small) sent through in the inverse direction*—conditions impossible completely to realize in practice when working by the "method of opposition" or with the potentiometer.

Effect of Temperature on the E.M.F. of Clark's Cell.

139. According to Clark (Proc. Roy. Soc. xx. p. 444), the E.M.F. of a hot-prepared mercurous zinc-sulphate cell diminishes at an approximately constant rate of 0·06 per cent. per degree rise in temperature between 15°·5 and 100°; he states, however, that this figure might be verified with advantage. A number of observations having indicated, as a preliminary result, that this value is considerably too high between the temperature-range (10° to 25°) most frequently obtaining in practice, and that fairly constant results are given with different cells, the following experiments were made in order to determine more exactly the mean coefficient of alteration per degree between these temperature-limits, with the result of showing that, instead of Clark's number (0·0006) being deduced, a value but little above two thirds of this figure was obtained, viz. ·000411, as the average of ten experiments with five cells.

Let the E.M.F. of a given cell, taken temporarily as a standard, be 1 at temperature t_1 (near to 15°), and let the E.M.F. of a second cell compared therewith be a_1 when the cell compared is at a temperature t_2 , the standard being still at t_1 . In another experiment, when the standard is at a temperature t_3 not far from t_1 , let the E.M.F. of the second cell be a_2 , this cell being at the temperature t_4 . Now let x be the mean coefficient of variation for 1° between t_2 and t_4 for the second cell, whilst x' is the analogous coefficient between t_1 and t_3 for the temporary standard. Then, since the E.M.F. of the standard at t_1 is unity, its E.M.F. at t_3 is $1 - (t_3 - t_1)x'$, whence the E.M.F. of the second cell at t_4 is $a_2\{1 - (t_3 - t_1)x'\}$. The E.M.F. of this second cell at t_4 , however, is also

$$a_1\{1 - (t_4 - t_2)x\};$$

so that

$$a_1\{1 - (t_4 - t_2)x\} = a_2\{1 - (t_3 - t_1)x'\}.$$

Now, from Clark's experiments and certain preliminary observations made by ourselves, it results that x is approximately equal to x' ; whilst if the temperatures are suitably chosen so that the mean of t_1 and t_3 is sensibly the same as the mean of t_2 and t_4 , it must result that the difference between x and x' is very small; and, finally, if t_1 and t_3 differ but little in comparison with the difference between t_2 and t_4 , any errors in the valuation of x' will be but small relatively. Hence, taking $x = x'$, it results that

$$x = \frac{a_1 - a_2}{a_1(t_4 - t_2) - a_2(t_3 - t_1)}.$$

In order, then, to determine x , it is only necessary to determine the relative readings of two cells, first when one is at t_1 and the other at t_2 (say at 15° and 0° respectively), and secondly when the first is at t_3 and the second at t_4 (say at 14° and 30° respectively), the temperatures being such that $t_1 + t_3$ approximately equals $t_2 + t_4$ (as in the case of the supposed numbers).

To carry out this principle two water-jacketed metal chambers were constructed, furnished with delicate thermometers reading to $0^\circ.01$ C., and containing respectively the sets of cells to be compared, the poles of the cells being connected with the mercury-cup arrangement applied to the electrometer by means of covered wires passing through narrow glass tubes fixed in the double lids of the chambers, so that no conducting contact between the wires themselves or between the wires and lids &c. was possible. One of the water-jackets was filled with water at near 15° , the other

with water either at or near 0° or at or near 30° , as the case might be; the masses of fluid (agitated from time to time with a peculiar stirrer) were so large that the temperature of the chamber-spaces varied but little during the progress of the series of readings ultimately made. The mean temperatures indicated by the thermometers during the series were taken as the mean temperatures of the cells (placed in the chambers some time before the readings were commenced, so as to attain sensibly the temperatures of the chamber-spaces). The readings were carried out in systematic order; so that the average reading for each cell should be exactly comparable with that of any other, notwithstanding any possible running-down of the electrometer-scale during the progress of the readings. For instance, if in the first chamber two cells (A and B) were placed, and in the second two others (C and D), the readings were alternately taken in the orders A, B, C, D and D, C, B, A, or C, D, A, B and B, A, D, C; so that the average reading for each cell was identical with that which would have been observed had the electrometer-scale value been absolutely constant throughout at its mean value (the actual variation of the electrometer-scale during any set of readings was considerably under 1 per cent.).

Thus, for instance, the following numbers were obtained in two experiments, in each of which the same two cells A and B were placed in the first chamber, and the same two (C and D) in the second:—

	1st experiment.	2nd experiment.
t_1	$16^{\circ}\cdot84$	$17^{\circ}\cdot04$
t_2	$1^{\circ}\cdot08$	$3^{\circ}\cdot30$
t_3	$9^{\circ}\cdot72$	$10^{\circ}\cdot98$
t_4	$26^{\circ}\cdot02$	$25^{\circ}\cdot12$
Average scale-reading for A and B taken together at t_1 }	$159\cdot94$	$159\cdot62$
Average reading for C at t_2	$161\cdot00$	$160\cdot75$
Average reading for A and B taken together at t_3 . }	$153\cdot00$	$152\cdot56$
Average reading of C at t_4	$152\cdot25$	$152\cdot00$
a_1 $\frac{161}{159\cdot94}$	$=1\cdot0066$	$\frac{160\cdot75}{159\cdot62}=1\cdot0071$
a_2 $\frac{152\cdot25}{153}$	$=\cdot9951$	$\frac{152}{152\cdot56}=\cdot9963$
$x = \frac{a_1 - a_2}{a_1(t_4 - t_2) - a_2(t_3 - t_1)}$	$\dots \cdot000358$	$\cdot000386$

Mean value of $x = \cdot000372$.

Similarly the values $\cdot 000439$ and $\cdot 000428$ (mean = $\cdot 000434$) were obtained for x in the case of cell D simultaneously examined. The following Table exhibits in brief these figures and those obtained in six other experiments with three other different cells:—

	1st experiment.	2nd experiment.	Mean.
1st cell . . .	$\cdot 000358$	$\cdot 000386$	$\cdot 000372$
2nd „ . . .	$\cdot 000439$	$\cdot 000428$	$\cdot 000434$
3rd „ . . .	$\cdot 000480$	$\cdot 000481$	$\cdot 000481$
4th „ . . .	$\cdot 000436$	$\cdot 000397$	$\cdot 000417$
5th „ . . .	$\cdot 000364$	$\cdot 000336$	$\cdot 000350$
General average . . .			$\cdot 000411$

Hence, finally, it results that the E.M.F. of a Clark's cell set up with saturated zinc-sulphate solution is, at a temperature t not more than 10° or 12° above or below $15^\circ 5$ C.,

$$1\cdot457\{1 - (t - 15^\circ 5) \times 0\cdot00041\} \text{ volt;}$$

it being admitted that Clark's valuation is exact, viz. $1\cdot457$ volt at $15^\circ 5$.

On the Work done during Electrolysis.

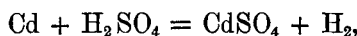
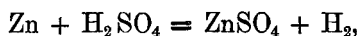
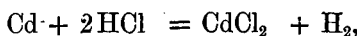
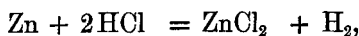
140. The experiments described in the previous portions of these researches have shown that, when a current is passed through an electrolytic cell, the amount of energy expended (positively or negatively) during the passage in performing a given amount of chemical work (apart from that transformed into heat in consequence of the resistance proper of the cell in accordance with Joule's law) is not constant, but *increases algebraically with the current-density*, in such wise that when the cell is an ordinary decomposing cell (*e. g.* a voltameter) the "counter electromotive force" of the cell increases in arithmetical value with the current-density, whilst when the cells is an electromotor (*i. e.* such a cell as to yield a *negative* counter E.M.F.), the arithmetical value of the negative counter E.M.F. (*i. e.* the direct E.M.F. of the cell) decreases with the current-density. The extra work done by a stronger current as compared with a weaker one in the former case, and the deficiency of work corresponding with the fall in direct E.M.F. in the latter case, make their appearance in the form of sensible heat in the cell.

Experiments have been published by Favre (*vide* Part I. §§ 14 and 15) which appear to show that certain forms of electromotor-cells can generate currents capable of doing more work externally to the cell than corresponds with the net chemical action taking place, this extra work being gained at

the expense of the sensible heat of the cell, which becomes cooled by the passage of a current of too small magnitude to generate, in accordance with Joule's law, sufficient heat in the cell to overpower this cooling action. Inasmuch, however, as the mercury-calorimeter was employed in these experiments of Favre, whilst, from the nature of the case, but feeble currents passed, so that the total amount of chemical action in a given time could be but small, it seems not unlikely that an excessively large probable error attends the numerical values obtained. In point of fact, one of the cells found by Favre to behave in this way was Grove's cell; and his results in this respect are totally at variance with all other experiments on the subject (compare H. F. Weber, *Phil. Mag.* 1878, v. p. 195), leading to the conclusion that the supposed cooling action was not a real effect, but simply the result of the accumulation of experimental errors. In order to see whether this was also the case with the other cells examined by Favre, the following experiments were made.

These other cells were simple voltaic couples of zinc and platinum or cadmium and platinum immersed in dilute hydrochloric acid; the numbers obtained by Favre as the cooling effects per gramme equivalent of metal dissolved were respectively 1051 and 1288 gramme-degrees, corresponding with $\cdot 046$ and $\cdot 057$ volt*. On the other hand, with dilute sulphuric acid in lieu of hydrochloric, Favre found that no cooling action was traceable, but that the cells were always warmed by the passage of a current. Now these results, if correct, must imply that the E.M.F. of a zinc-platinum or a cadmium-platinum cell, when generating only a minute current, is above the value corresponding with the heat-development due to the net chemical action taking place when hydrochloric-acid solution is the exciting fluid, and below that value when dilute sulphuric acid is used instead; *i. e.* the electromotive forces of cells containing dilute hydrochloric acid must be above $\cdot 754$ and $\cdot 388$ volt respectively with zinc-platinum and cadmium-platinum couples, and the electromotive forces of cells containing dilute sulphuric acid must be below $\cdot 835$ and $\cdot 470$ volt respectively with these same couples, these being the values in E.M.F. corresponding respectively with the heat-developments per gramme-equivalent in the reactions

* For the sake of comparison with the experiments described in the previous portions of these researches, the factor 4410 for converting gramme-degrees into volts is adhered to, notwithstanding that the balance of evidence now seems to indicate that the value of J hitherto assumed (42 megalergs) is somewhat too high, and that the B.A. unit of resistance is upwards of 1 per cent. below its intended value, instead of being exact as hitherto assumed.



these heat-developments being, per gramme-molecule, as follows* :—

Zn, Cl ₂ , aq.	= 112840	Cd, Cl ₂ , aq.	= 96250
H ₂ , Cl ₂ , aq.	= 78640	H ₂ , Cl ₂ , aq.	= 78640
Difference	34200	Difference	17610
Diff. per gramme-equi- valent	17100	Diff. per gramme-equi- valent	8805
Corresponding with volt	·754	Corresponding with volt	·388
Zn, O, SO ₃ , aq.	= 106090	Cd, O, SO ₃ , aq.	= 89500
H ₂ , O	= 68200	H ₂ , O	= 68200
Difference	37890	Difference	21300
Diff. per gramme-equi- valent	18945	Diff. per gramme-equi- valent	10650
Corresponding with volt	·835	Corresponding with volt	·470

141. In order to see whether the electromotive forces actually developed by these four voltaic combinations are really above the calculated values in the first two cases and below in the second two instances, when the disturbing effects of dissolved air are eliminated, cells were set up like those described in § 85, and caused to generate feeble currents by employing large external resistances. In all cases it was found that when the errors due to dissolved air were eliminated and the readings became constant, the E.M.F. actually developed *invariably fell short of the value corresponding with the net chemical action* by an amount which increased with the current-density until the reduction became a large fraction of the E.M.F. observed with the smallest possible densities. With hydrochloric-acid cells the deficiency was not so great in the first instance, and

* These figures are deduced from Julius Thomsen's thermochemical data and the mean value for the heat of formation of water arrived at in § 31. Thomsen's values relate to the degree of dilution MCl_2 , 400 H_2O , and MSO_4 , 400 H_2O . Some experiments made by us on the amounts of heat evolved on diluting stronger solutions of zinc and cadmium chlorides and sulphates indicate that these values require slight corrections for stronger solutions than those used by Thomsen; but the alterations thus produced in the net heat-development and in the E.M.F. corresponding thereto is but small.

the rate of increase in deficiency was not so rapid, as with sulphuric-acid cells. Thus the following four experiments may be cited as illustrations of the results obtained in numerous cases:—

Hydrochloric Acid : Zinc and Platinum.				
Current, in microampères, = C.	Current-density, in microampères, per square centimetre.	Observed differences of potential between plates = E.	Value of CR.	E.M.F. of cell, $e = E + CR$.
12.6	1.6	.633633
23.4	2.9	.628	.001	.629
55.1	6.9	.609	.002	.611
102.4	12.8	.585	.003	.588
224.5	28.1	.545	.007	.552
Calculated E.M.F. = .754				
Hydrochloric Acid : Cadmium and Platinum.				
6.5	0.8	.347347
11.0	1.4	.291	.001	.292
14.8	1.85	.249	.001	.250
33.7	4.2	.161	.003	.164
54.3	6.8	.130	.005	.135
97.8	12.2	.103	.010	.113
Calculated E.M.F. = .388				
Sulphuric Acid : Zinc and Platinum.				
12.6	1.6	.626626
23.4	2.9	.540	.001	.541
55.1	6.9	.492	.002	.494
102.4	12.8	.439	.003	.442
224.5	28.1	.353	.007	.360
Calculated E.M.F. = .835				
Sulphuric Acid : Cadmium and Platinum.				
6.5	0.8	.301301
11.0	1.4	.259	.001	.260
14.8	1.85	.211	.001	.212
33.7	4.2	.080	.003	.083
54.3	6.8	.033	.005	.038
97.8	12.2	.019	.010	.029
Calculated E.M.F. =470				

In each of these experiments the plate-surface was constantly 8 square centimetres ; the hydrochloric-acid solution

was close to 2HCl , $50\text{H}_2\text{O}$ and 2HCl , $100\text{H}_2\text{O}$ in the first and second experiments respectively, and the sulphuric-acid H_2SO_4 , $50\text{H}_2\text{O}$ and H_2SO_4 , $100\text{H}_2\text{O}$ in the third and fourth experiments respectively. The zinc plates were amalgamated, the cadmium ones not.

142. The experiments described in Parts IV., V., and VI. indicate that the amount of diminution brought about in the E.M.F. of an electromotor (either a simple cell, or one after Daniell's construction) by an increase in the current-density may readily greatly exceed any possible effect due to the accumulation round the two plates of fluids of widely different molecular strength, and, further, that, as a general rule, the effect of diminishing the area of the plate on which the metal is deposited is considerably greater than that of a similar diminution in the area of the other plate, although this is not invariably the case. It is hence evident that the chief source of nonadjuvancy especially lies in the incomplete manifestation as electricity of the energy due, after the elimination by the action of the current of the deposited metal (or body equivalent thereto) in the nascent form, to the subsequent transformation thereof into the permanent form. Clearly the same kind of thing must be equally true for the other products of electrolysis evolved at the other electrode. Hence the reason why a less amount of non-adjuvancy is brought about at this side is presumably the greater amount of attraction exercised by the material of the electrode for the nascent product ("sulphion" of Daniell in the case of cells containing sulphates) here evolved, owing to their opposite chemical characters, than is observable at the other electrode. Admitting this to be so, it should result that the more oxidizable the metal dissolved (*i. e.* the greater the heat of formation of the compound produced by its solution), the less will be the amount of nonadjuvancy due to the incomplete conversion into electricity at this plate of the energy due to transformation of nascent into final products. The results of the experiments hitherto described, however, being complicated by the formation of solutions of different strengths around the two plates, are not sufficiently precise to show that, under given conditions, a zinc plate, for example, causes less nonadjuvancy than a cadmium one, and so on. Accordingly the following experiments on the point were made, the result of which is to show indisputably that the more oxidizable the metal the less the nonadjuvancy.

An electrolytic cell was constructed, consisting of a wide glass tube closed by india-rubber bungs through which passed wires terminating interiorly in the plates to be experimented with, the opposed plate-surfaces being perpendicular to the

axis of the tube and therefore parallel to one another, and the anterior portions of the plates and the wires being thickly coated with gutta-percha. The tube was then filled, for instance, with concentrated zinc-sulphate solution, with plates of zinc at an accurately known distance apart, and was kept at a temperature sensibly uniform. A series of currents of various strengths was then passed through the cell, and the difference of potential subsisting between the plates determined in each case. These values represented the numerical values of $e_1 + CR$, where e_1 is the counter E.M.F. set up during the electrolysis, C the current, and R the resistance of the cell; and from them the values of this expression for definite values of C (50, 100, 200 microampères, &c.) were readily calculated by interpolation. The + zinc electrode was then removed, and a copper plate exposing exactly the same area placed in precisely the same position. The observations were then repeated, the temperature being the same as before, and a new series of values, $e_2 + CR$, calculated, e_2 being the counter E.M.F. now set up for a given value of C . Since R is constant throughout, it is evident that the difference between the two values for a given current obtained, first with a zinc, and secondly with a copper + electrode, represents $e_2 - e_1$. Now necessarily both e_1 and e_2 increase with the value of C in accordance with the general law to that effect deduced from all the previous observations (§ 133); but if it be true that a less production of heat instead of electricity is brought about when nascent sulphur is liberated in contact with zinc than when in contact with copper, e_1 must increase less rapidly with the current than e_2 , and hence the value of $e_2 - e_1$ must rise with the current-strength. Precisely this result was observed in every case: for example, the following numbers were obtained in a pair of sets of observations carried out as described, the area of the plates being 0.50 square centim. throughout.

+ Zinc electrode.		+ Copper electrode.	
C.G.S. current.	Observed potential-difference.	C.G.S. current.	Observed potential-difference.
·00000436	·018	00000466	1·073
·00000866	·039	00000883	1·089
·00001432	·062	00001460	1·127
·00002130	·091	00002275	1·159
·00004160	·174	00004450	1·251

From these figures the following are obtained by interpolation:—

Current.	Potential-difference.		
	+ Zinc.	+ Copper.	$e_2 - e_1$.
·000005	·021	1·075	1·054
·00001	·045	1·101	1·056
·00002	·085	1·147	1·062
·00004	·168	1·232	1·064

Precisely similar results were obtained in numerous other analogous experiments. Thus the following Table illustrates some of the figures obtained, the + zinc plate originally employed being replaced by a plate of the same size, I. of bright copper, II. of electro-copper, III. of amalgamated copper, IV. of bright cadmium, V. of bright silver.

C.G.S. current.	Values of $e_2 - e_1$ obtained.				
	I.	II.	III.	IV.	V.
·000005	1·063	1·054	1·065	1·486
·00001	1·067	1·057	1·076	1·498
·00002	1·073	1·061	1·084	·315	1·503
·00004	1·075	1·068	1·099	·324	1·512

143. A still better illustration of the regular rise in value of $e_2 - e_1$ with the current is afforded by the following series of numbers obtained as the average results of several sets of observations very carefully made—A with a bright zinc + electrode, B with one of bright cadmium, C with one of bright copper, and D with one of bright silver. In every case the mean temperature was the same within two or three tenths of a degree (varying from $17^{\circ}55$ to $17^{\circ}9$ throughout). In the last case it was found that, whilst perfectly steady readings could be obtained with current-strengths up to something like ·0007, with higher strengths this was no longer the case, silver peroxide being apparently formed instead of silver sulphate. In these experiments all the plates exposed an area of $1\frac{1}{2}$ square centim., the solution electrolyzed being a nearly saturated one of pure zinc sulphate, renewed for each series; the plates were about 5 centim. apart, the tube holding them being 3 centim. in internal diameter.

C.G.S. current.	Difference of potential set up.			
	A.	B.	C.	D.
·00002	·029	·317	1·069	1·490
·00005	·044	·334	1·086	1·509
·0001	·063	·354	1·107	1·530
·0002	·084	·381	1·139	1·562
·0005	·146	·451	1·210	1·636
·001	·230	·547	1·310	
·0015	·311	·636	1·403	
·002	·389	·730	1·498	
·0025	·476	·830	1·598	

These figures yield the following six sets of values of $e_2 - e_1$ for the corresponding pairs of + electrodes compared.

Current.	Zinc-cadmium.	Zinc-copper.	Zinc-silver.	Cadmium-copper.	Cadmium-silver.	Copper-silver.
·00002	·288	1·040	1·461	·752	1·173	·421
·00005	·290	1·042	1·465	·752	1·175	·423
·0001	·291	1·044	1·467	·753	1·176	·423
·0002	·297	1·055	1·478	·758	1·181	·423
·0005	·305	1·064	1·490	·759	1·185	·426
·001	·317	1·080	·763		
·0015	·325	1·092	·767		
·002	·341	1·109	·768		
·0025	·354	1·122	·768		

Not only does the value of $e_2 - e_1$ increase with the current-density in every case, but, further, the rate of increase is greater when zinc is compared with silver than with copper, and greater then than when compared with cadmium; similarly the rate of increase with cadmium and silver is greater than with copper and silver, and so on. It is further noticeable that in each case a value of $e_2 - e_1$ with some particular current-strength is deducible which is sensibly the same as the E.M.F. of a cell after Daniell's construction containing the same metals and sulphate solutions of equal molecular strength; so that in general it may be said that, for a current-density below a particular limit, the value of $e_2 - e_1$ is less than that of the corresponding Daniell form of cell, whilst for a current-density above this limit it is greater.

144. The following experiment seems to show that the substitution of dilute sulphuric acid for zinc-sulphate solution as the electrolyte makes no material difference in the end result, the — electrode being made of platinum, and the disturbing influence of dissolved air being eliminated. Two precisely similar U-tube cells (§ 85) were filled with recently boiled dilute sulphuric acid (11·5 grammes H_2SO_4 per 100 cubic centim.), and

fitted with uniformly sized plates (8 square centim. total surface in each case) at an equal distance asunder, so that the resistance of the cell should be sensibly the same in each case. In the first cell the plates were of zinc (amalgamated) and platinum, and in the second of copper and platinum respectively; the two were arranged in series with a couple of Leclanché cells, so that the platinum plates were necessarily the — electrodes; a large variable resistance being included in the circuit, the current could be regulated at pleasure. A current of some fifty microampères being sent through for three days, the readings became steady when all the dissolved air around the platinum plates was eliminated; the current was then varied from time to time, and a series of readings of the potential-difference between each pair of plates taken. By interpolation as before, the following figures were then deduced from the average values.

Current in micro-ampères.	Micro-ampères per square centim.	Difference of potential.		$e_2 - e_1$.
		+ zinc.	+ copper.	
20	2.5	— .552	+ .449	+ 1.001
40	5.0	— .558	+ .448	+ 1.006
80	10.0	— .498	+ .521	+ 1.019

The value of $e_2 - e_1$ consequently increases with the current-density as before. The numerical values observed in this experiment are somewhat lower than those found in the experiments above described, as might be expected, since the largest current-density employed in this case, being only 10 microampères per square centim., is considerably below the smallest cited in the previous observations, in the last of which a minimum current of .00002 C.G.S. units (or 200 microampères) was employed with plate-surfaces of 1.5 square centim., giving a density of 133.3 microampères per square centim., in which case the value of $e_2 - e_1$ was 1.040; whilst in the former experiments a minimum current of .000005 C.G.S. unit (50 microampères) was employed with a plate-surface of .50 square centim., giving a density of 100 microampères per square centim., when values of from 1.054 to 1.065 were observed.

145. Some experiments were also made with analogous pairs of cells in which the + electrodes were made of metals not attacked by the nascent products arising from the electrolysis of sulphates, *e. g.* gold and platinum. In these instances it was found that platinum behaved in reference to gold just

as a more readily to a less readily oxidizable metal, this result being evidently brought about by the superior surface condensing-power possessed by platinum, in virtue of which a greater proportion of the energy due to the transformation of the nascent into the final products of electrolysis evolved at the + electrode becomes adjuvant. For instance, the following numbers were obtained with a pair of precisely similar cells containing the same copper-sulphate solution and copper — electrodes.

Current-density, microamperes per square centimetre.	Difference of potential between plates.		Difference.
	+Platinum.	+Gold.	
3.0	1.500	1.555	.055
7.0	1.534	1.591	.057
11.0	1.570	1.630	.060

Even with the lowest current-density and with platinum as + electrode the total amount of nonadjuvancy was here considerable; for the E.M.F. corresponding with the net chemical action is only 1.234 volt ($\frac{1}{2}[\text{Cu}, \text{O}, \text{SO}_3 \text{ aq}] = 27,980$ gramme-degrees = 1.234 volt); and the minimum difference of potential set up, after correction for the resistance of the cell (*i. e.* the counter E.M.F. set up, or the value of the term e in the expression $E = e + CR$), exceeds 1.490, since the term CR in this case was much less than .010 volt.

In just the same kind of way, when platinum and gold were respectively made the — electrodes in similar pairs of cells containing dilute sulphuric acid and a constant oxidizable + electrode, the superior surface condensing-power possessed by platinum caused a less degree of nonadjuvancy during the transformation of nascent into free hydrogen. Thus, for example, the following numbers were obtained with a copper + electrode and acid containing 10 per cent. of $\text{H}_2 \text{SO}_4$.

Current-density, microamperes per square centimetre.	Difference of potential between plates.		Difference.
	—Platinum.	—Gold.	
2.5	.449	.575	.126
5.0	.488	.619	.131
10.0	.521	.661	.140

Here again, even in the most favourable instance, with the smallest current-density and platinum as — electrode, a considerable amount of nonadjuvancy subsisted; for the value of CR in this case was not greater than .001; so that the minimum counter E.M.F. set up was at least .448 volt, whilst the E.M.F. corresponding to the net chemical action is only .270 volt, the heat-development being per gramme equivalent

$$\begin{array}{rcl} \frac{1}{2}(\text{H}_2, \text{O}) & . & = 34100 \text{ gramme-degrees.} \\ \frac{1}{2}(\text{Cu}, \text{O}, \text{SO}_3 \text{ aq}) & = 27980 & \text{,,} \text{,,} \\ \hline & 6120 & \text{,,} \text{,,} = .270 \text{ volt.} \end{array}$$

It is hence evident, *à fortiori*, that when acidulated water is decomposed with two gold electrodes, the counter E.M.F. set up must be much greater for a given current-density than when two platinum electrodes are used, the deficiency in condensing-power being then manifest at both electrodes simultaneously. The experiments described in Part IV. § 90 have shown that this is the case.

146. In addition to the experiments above described as examples, a large number of analogous observations have been made with varying kinds of electrolytic solutions and electrodes, and with varying strengths of solutions. The general results of these experiments, so far as at present completed, may be thus summarized.

(1) When an electrolytic cell is of such a nature that the counter E.M.F. set up is negative (*i. e.* when the cell is an electromotor), it is always found that the *E.M.F. developed is less the greater the density of the current generated*. With very small current-densities the E.M.F. has a maximum value which in certain cases (*e. g.* Daniell's cell and the analogous zinc-cadmium and cadmium-copper cells described in Part VI.) is substantially identical with the E.M.F. corresponding with the heat-development due to the net chemical action taking place in the cell, *i. e.* with the E.M.F. representing the algebraic sum of the chemical affinities involved. In certain other cases (*e. g.* the zinc-silver, cadmium-silver, and copper-silver cells described in Part VI.) the maximum E.M.F. developed is sensibly *below* that due to the net chemical action.

(2) Some kinds of combinations have been found to be capable of existing which can develop a *greater* E.M.F. than that due to the net chemical action (although the particular cells described by Favre as possessing this property are not really cases in point, Favre's results being due to experimental errors); amongst such combinations may be mentioned several where *lead* is the metal dissolved, *i. e.* lead-copper cells

charged with solutions of acetates. It is noticeable that in such cases Volta's law of summation holds, the sum of the electromotive forces of two cells, one containing zinc and lead and the other lead and copper, being equal to the E.M.F. of a zinc-copper cell, the E.M.F. of the first cell being just as much below the amount calculated from the heat-development as that of the second is above the amount similarly calculated. This class of cells is now undergoing careful examination, and will be dealt with in a subsequent paper. Unfortunately, progress in this direction during the last fifteen months has been greatly retarded by the refusal of the Administrators of the Government Fund of £4000 to continue the grants by the aid of which the previous portions of these researches have mainly been made, on account of which circumstance numerous other points of interest that have cropped up have necessarily remained uninvestigated*.

(3) When the electrolytic cell is not an electromotor, the counter E.M.F. set up (positive) always *increases in amount with the current-density*. When the + electrode is of such a nature as to combine with the products of electrolysis evolved thereat, other things being the same, *the rate of increase is slower the greater the chemical affinity* between the nascent products of electrolysis evolved at the + electrode and the material of which that electrode is composed; *i. e.* the greater the affinity, the less the degree of nonadjustancy brought about at the + electrode.

(4) Whether the cell be an electromotor or not, there is always (with currents not so small as to be practically infinitesimal) a greater or less degree of nonadjustancy brought about at the - electrode, owing to the development of heat in lieu of electricity during the transformation of nascent into ultimate permanent products of electrolysis. In many cases this source of nonadjustancy decidedly predominates over that at the + electrode.

(5) The particular extent to which the nonadjustancy reaches at either electrode appears to be a complex function not only of the chemical nature of the electrode, the physical conditions of its surface, and the character of the nascent products of electrolysis evolved thereat, but also of the temperature, and the degree of concentration of the solution electrolyzed, and

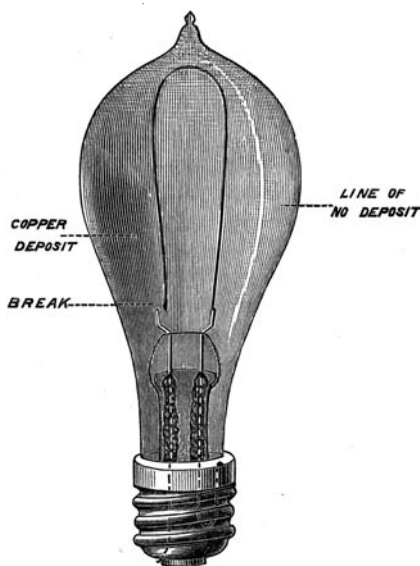
* Since the presentation to the Physical Society of Part VI. of these researches, a paper has appeared by F. Braun (*Annalen der Phys. u. Chem.* xvi. p. 561), in which the author shows that various combinations examined by him give electromotive forces sensibly the same as those calculated from thermochemical data, whilst others fall short of, and some exceed, the calculated values.

possibly of other conditions besides. Other things being equal, it appears to be a general rule that *the weaker the solution, the greater the degree of nonadjuvancy*. When a gas is one of the permanent products of electrolysis at either electrode, *the greater the surface condensing-power of the material of which the electrode is composed, the less is the degree of non-adjuvancy*.

VI. On a Phenomenon of Molecular Radiation in Incandescence Lamps. By J. A. FLEMING, B.A., D.Sc.*

NOT long ago a curious phenomenon came under my notice in connexion with the burning of Edison incandescence lamps, which presents sufficient interest to warrant my drawing the attention of physicists to it.

As is well known, the carbon filament in the Edison lamp is of a horse-shoe form. The two extremities of the loop are



clamped into small copper clamps on the ends of the platinum wires, which are sealed through the glass. The ends of the carbon loop are electroplated over with copper at the place where they are connected to the clamp in order to make a

* Communicated by the Physical Society, having been read at the Meeting on May 26, 1883.