

## On the Determination of Chemical Affinity in terms of Electromotive Force - Part VIII

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VIII. *On the Determination of Chemical Affinity in terms of Electromotive Force.*—Part VIII. 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\**.

[Plate V.]

*On the Electromotive Force set up during Interdiffusion.*

147. It is well known that the E.M.F.'s of cells like those of Daniell and of Grove vary with the degree of concentration of the solutions used therein, and many measurements of the amounts of such variations have been from time to time published by different experimenters, *e.g.* by Regnault (*Ann. de Chim. et de Phys.* [3] xliv. p. 453), Svanberg (*Pogg. Annalen*, lxxiii. p. 290 [1848]); and more recently by Streintz (*Carl. Rep.* xv. p. 6 [1879]), Baumgartner (*ibid.* xv. p. 105 [1879]), and Fromme (*Annalen der Physik*, viii. p. 326 [1879]). From various causes, the nature of which will be apparent later on, the figures obtained by different observers do not exhibit such a degree of concordance as to lead to the establishment of any fundamental principle coordinating the variation in E.M.F. with the degree of dilution of the solutions used, excepting this

\* Read January 26, 1884.

Fig. 1.

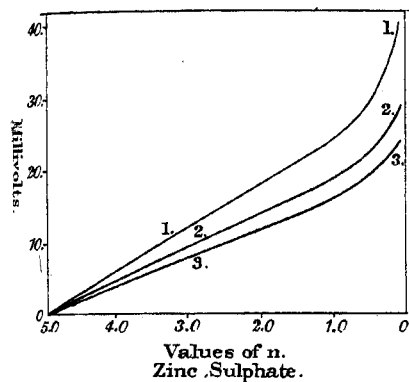


Fig. 2.

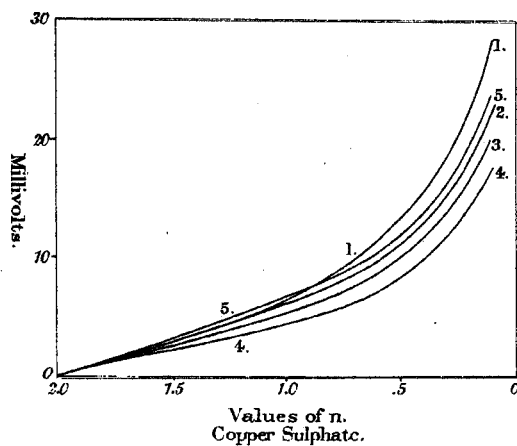


Fig. 3.

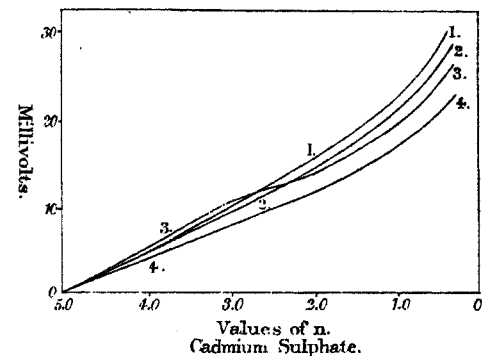


Fig. 4.

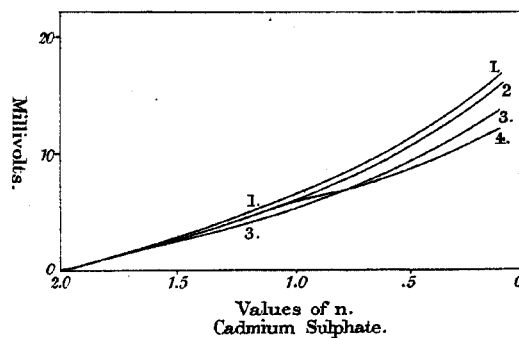


Fig. 5.

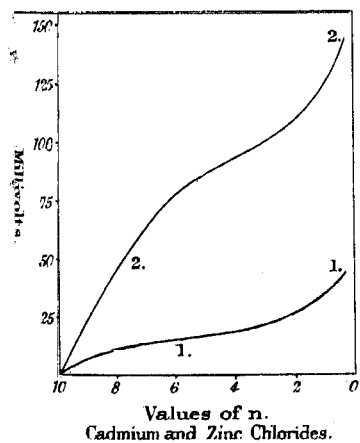


Fig. 6.

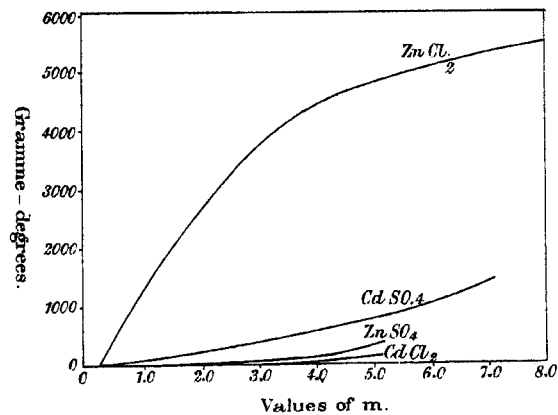
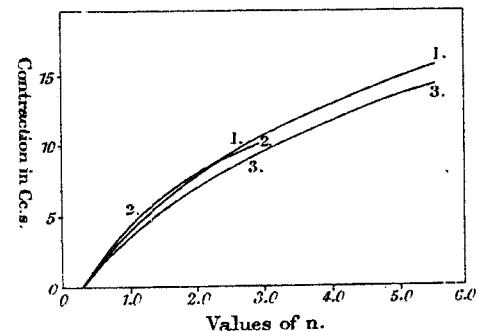


Fig. 7.



general rule, that when the strength of the copper sulphate in a Daniell cell or of the nitric acid in a Grove's cell is decreased, a fall in the E.M.F. results; and that when the strength of the solution surrounding the zinc is decreased, a rise in E.M.F. ensues, provided the solution is one of zinc sulphate: with other salts, and with dilute sulphuric acid, some observations indicate rise, others fall, in E.M.F. with decrease of strength.

It has been shown by Moser (*Annalen der Physik*, iii. p. 216 [1878]) that when two solutions of the same metallic salt, but of unequal strengths, are allowed to communicate so as to mix by interdiffusion, a current is set up passing from the weaker to the stronger solution through the fluid when electrodes are employed of the metal contained in the salt used (*e.g.* zinc for solutions of zinc sulphate, copper for solutions of copper sulphate, and so on); whilst the experiments described in Part V. (§ 110) indicate that the variations in E.M.F. of a Daniell cell containing zinc-sulphate solution round the zinc, according as the zinc-sulphate or the copper-sulphate solution varies in strength, are approximately equal numerically to the values obtained by Moser as the E.M.F.'s set up by the interdiffusion of solutions of zinc sulphate or of copper sulphate respectively, with the same limits of strength of solution.

It seemed of interest to pursue this point further, so as to decide by accurate measurements how far this approximation is merely an accidental coincidence: accordingly a large number of experiments have been made, mostly described in the following pages.

At first the observations were made by means of the quadrant electrometer, no permanent current passing; but it was found that the experimental and observational errors were such that unless a very large number of duplicate cells were prepared and very many observations made with each, involving an immense expenditure of labour and time, trustworthy averages could not be obtained. The electrometer-readings (deflections on both sides of zero) could, at best, be read to no nearer than  $\pm 0.0025$  volt; so that averages for single-cell values with a probable error of not more than  $\pm 0.001$  volt (one millivolt) entailed a large number of readings for each cell; and as the values for different cells thus obtained exhi-

bited a range of several millivolts, numerous duplicate cells had to be set up to obtain a final mean with a probable error of less than  $\pm 1$  millivolt as the E.M.F. of each kind of cell; whilst, finally, the differences between the mean E.M.F.'s thus obtained exhibited, when plotted, deviations from a regular mean curve approaching to  $\pm 1$  millivolt, even with the utmost care in making observations and the bestowal of much time in so doing. Accordingly, the method of observation was changed, a delicate galvanometer being substituted for the electrometer; the instrumental errors being smaller and the sensitiveness greater\*, the same degree of accuracy (*i. e.* the same limits of probable error) were found to be attainable with a notably smaller number of observations, provided that certain precautions were observed, detailed more fully later on (§§ 149, 150). It was soon found, however, that the observance of these precautions sufficed to permit of the method of opposition being used so as to obtain directly the difference in E.M.F. between two cells alike in all respects, save that the zinc (or copper) sulphate solution used in one was stronger than that in the other. The values thus obtained led to sensibly the same mean curves as those obtained with a far greater amount of labour by means of the electrometer, and, notwithstanding the diminution in the number of observations, the range of probable error was sensibly diminished.

\* The galvanometer (by Elliott) was capable of being adjusted so as to give a total deflection, reading on both sides of zero with a reversing-key, of upwards of 200 scale-divisions when the current from a Daniell cell was passed through a resistance of 100,000 ohms, using the  $\frac{1}{1000}$  shunt; so that one scale-division =  $\frac{1.114}{1000 \times 100,000 \times 200}$  ampere = 0.00056 micro-ampere.

It being convenient to have some term representing the millionth of a millionth ( $0.000000000001 = 10^{-12}$ ), it is proposed to use the prefix "elasso" for this purpose (from *ελασσον*), just as "micro" represents  $10^{-6}$ , and "mega" represents  $10^6$ : the value of 1 scale-division as above then becomes 56 *elasso-amperes*. The fraction  $0.000000001 = 10^{-9}$  may be conveniently represented by the double prefix "milli-micro," using each half in its ordinary sense; so that a centimetre = 1 *milli-micro earth-quadrant*. In the same kind of way 1,000,000,000 ohms may be termed a *kilomegohm*; and a million of million ergs may be spoken of as a *meizery* (*μείζων*). This nomenclature seems to be practically more convenient than such terms as twelfth-ampere, ohm-nine, erg-twelve, &c.

One of the essential precautions being the avoidance of diminution in E.M.F. in consequence of so-called "polarization," by using currents of only minute density, it at once suggested itself that under these conditions in all probability the difference of potential set up between (for example) two plates of zinc immersed in zinc-sulphate solutions of different strengths allowed to intermingle by interdiffusion (or what may be conveniently called a *diffusion-cell*) would vary little, if at all, from that set up between the same two plates immersed in the same solutions respectively when these solutions are not directly connected so as to interdiffuse, but are severally connected (by any of the means used in two-fluid cells) with solutions of copper sulphate of identical strengths, in which are immersed copper plates of the same surface-character connected together by a wire : *i. e.* that subsisting between the terminal plates of two opposed Daniell cells containing the same copper-sulphate solution, but zinc solutions differing from each other in strength and respectively identical with those used in the diffusion-cell, when the copper plates are united together and the zinc plates are the terminals. On trying the experiment this was found to be the case, *sensibly identical mean curves being obtained for given variations in solution-strength and for given kinds of plate-surfaces, whether the method of opposition was used, or that of diffusion-cells.*

148. Whichever method of observation was employed, the following general laws were always verified with a high degree of exactitude whenever sufficient observations were taken to get average results with only a small probable error. All the observations were carried out in every instance at a temperature within a very few degrees of  $18^{\circ}$  C., almost invariably between  $15^{\circ}$  and  $20^{\circ}$ .

(1) In any two-fluid cell containing solutions of two metallic salts and plates of the respective metals contained therein, an *increase in strength of the solution surrounding the plate acquiring the higher potential, in virtue of the normal action of the cell (i.e. the plate functioning as the copper plate of a Daniell cell), causes an increment in the potential-difference set up between that plate and the other.* The opposite effect is always produced by an increase in the strength of the solution surrounding the other plate. The increment and decrement

thus producible are, in certain cases, very considerable: with a Daniell cell a difference of nearly 6 centivolts (or upwards of 5 per cent. of the total E.M.F.) is producible, according as strong copper-sulphate and weak zinc-sulphate solutions are taken, or *vice versa*; with cells containing zinc and cadmium chlorides analogous differences up to even 30 centivolts are thus producible.

(2) A "law of summation" holds, expressible thus:—*The effect of the sum of a series of changes in the strengths of the solutions in a two-fluid cell is equal to the algebraic sum of the effects of each change severally.* Thus, by increasing the strength of the copper-sulphate solution in a Daniell cell (from, say,  $\cdot 25 \text{ CuSO}_4 \cdot 100 \text{ H}_2\text{O}$  \* to  $2\cdot 0 \text{ CuSO}_4 \cdot 100 \text{ H}_2\text{O}$ ), a given increment in E.M.F. ensues,  $=a$ : by similarly varying the zinc-sulphate solution (from, say,  $\cdot 25 \text{ ZnSO}_4 \cdot 100 \text{ H}_2\text{O}$  to  $5\cdot 0 \text{ ZnSO}_4 \cdot 100 \text{ H}_2\text{O}$ ), a decrement ensues,  $=b$ . Then the difference in E.M.F. between two cells, one containing  $\cdot 25 \text{ CuSO}_4 \cdot 100 \text{ H}_2\text{O}$  and  $\cdot 25 \text{ ZnSO}_4 \cdot 100 \text{ H}_2\text{O}$ , and the other containing  $2\cdot 0 \text{ CuSO}_4 \cdot 100 \text{ H}_2\text{O}$ , and  $5\cdot 0 \text{ ZnSO}_4 \cdot 100 \text{ H}_2\text{O}$ , is the sum of these amounts, *i. e.* is  $a-b$ ; so that if  $e$  is the E.M.F. of the first and  $E$  that of the second,  $E=e+a-b$ .

Similarly, if three cells be compared, alike in all respects save that the copper-sulphate solutions have (for example) the strengths  $\cdot 25 \text{ CuSO}_4$ ,  $1\cdot 0 \text{ CuSO}_4$ , and  $2\cdot 0 \text{ CuSO}_4$  (per  $100 \text{ H}_2\text{O}$  in each case), the excess of E.M.F. of the second over the first being experimentally found  $=c$ , and that of the third over the second being similarly found  $=d$ , then  $a=c+d$ .

(3) The values of  $a, b, c, d, \dots$  are independent, not only of the actual strength of the solution which does not vary in any two cells compared, but also of the nature of that solution and of the metal immersed in it.

For example, in zinc-copper-sulphate cells with amalgamated zinc and electro-copper plates, the effect of a given alteration in the strength of the zinc-sulphate solution is sensibly the same whether the copper-sulphate solution be strong or weak; and, further, is precisely the same in zinc-cadmium-sulphate, or in zinc-silver-sulphate cells set up with amalga-

\* Instead of expressing molecular strengths in the form  $\text{MSO}_4, n\text{H}_2\text{O}$ , and so on, it is more convenient for certain purposes to express them in the form  $m\text{MSO}_4, 100\text{H}_2\text{O}$ , and so on.

ated zinc plates. Similarly, the numerical value of the effect of a given alteration in the strength of the copper-sulphate solution is the same whether the zinc-sulphate solution be strong or weak ; and, further, is still the same in copper-cadmium-sulphate or copper-silver-sulphate cells set up with electro-copper plates \*.

(4) The values of  $a, b, c, d, \dots$  vary perceptibly with the nature of the plate-surface of the metal immersed in the varying solution ; *i. e.* they are not constant for a given difference in strength if the plate-surface vary. In the case of the metals copper, zinc, and cadmium the highest values are observed, *cæteris paribus*, with plates superficially amalgamated, the amalgam being *fluid* ; plates freshly electro-coated give lower values, and bright polished plates of fused metal lower values still.

(5) With the majority of kinds of plate-surface examined, the values of  $a$  and  $b$  in the expression

$$E = e + a - b$$

are such that  $a$  and  $b$  are unequal in magnitude for equal amounts of variation in the strength of the two solutions in a two-fluid cell. Sometimes  $a$  increases more rapidly than  $b$  in numerical value as the solution-strength increases ; in which case the E.M.F. of the combination rises with the strength of the solutions when both are always of equal molecular strength : such a case is presented by a zinc-copper-sulphate cell with electro-zinc and amalgamated copper plates (§ 154). Sometimes the opposite is the case, *e. g.* a zinc-cadmium-chloride cell with amalgamated zinc and electro-cadmium plates (§ 156). Zinc-copper-sulphate cells set up with amalgamated zinc and electro-copper plates show the peculiarity that  $a$  and  $b$  are nearly equal numerically for all solution-strengths ; so that the E.M.F. of such a Daniell cell is *practically invariable no matter what the strength of the solutions of zinc and copper sulphate used, provided that these are of the same molecular strength.*

(6) On contrasting the values of  $a, b, c, d, \dots$  with the

\* In copper-silver-sulphate cells the effect of a given increment in the strength of copper-sulphate solution is, of course, to *diminish* the E.M.F. of the cell, and not to increase it as in zinc-copper-sulphate cells.

E.M.F.'s corresponding to the amounts of heat developed on intermixture of grammes equivalents of the two strengths of the varying solution compared together, *the former are usually found to exceed the latter*, sometimes by a very considerable amount.

149. In carrying out observations by means of either the method of opposition or that of diffusion-cells, it is obvious that the current observed produced through a given total resistance only represents the E.M.F. due to difference of solution-strength, provided that the two zinc plates and the two copper plates are identical in surface-characters, and provided also that the current-density is small enough to reduce polarization to negligible amounts. In practice it is impossible to ensure equality of surface with any pair of plates, even though prepared with the greatest care in precisely the same way from the same mass; and the result is that when two plates, apparently identical, are immersed in the same solution, one is sufficiently electropositive with reference to the other to cause a distinctly measurable current to flow through even a large external resistance. In order to form some estimate as to the probable magnitude of this source of error, a large number of observations were made with pairs of zinc plates immersed in zinc-sulphate solutions of varying strengths, and pairs of copper plates immersed in copper-sulphate solutions. The following results in millivolts were obtained with upwards of 120 pairs of plates, readings being taken every few minutes for about half an hour after the first immersion, and being then averaged. As a rule the currents observed increased somewhat as time elapsed, so that the first readings were usually the minima. The galvanometer-readings were translated into volts by means of the formula

$$e = \frac{m}{n} \cdot \frac{R_2}{R_1} \cdot \frac{D}{1000} = m R_2 \cdot C,$$

where  $m$  = the galvanometer-reading to be translated (no shunt being used).

$n$  = the galvanometer-reading when a Daniell cell of E.M.F.  $D$  is used to send a current through a total resistance  $R_1$  ohms, employing  $\frac{1}{1000}$  shunt.

$R_2$  = total resistance in circuit when the reading  $m$  is taken.

$C$  = current representing 1 scale-division =  $\frac{D}{1000nR_1}$  amperes.

If the potential differences are expressed in millivolts, then

$$e = \frac{m}{n} \cdot \frac{R_2}{R_1} \cdot D.$$

Bright Zinc Plates.			
Molecular strength of solution, per 100 H <sub>2</sub> O.	Near 5 MSO <sub>4</sub> .	MSO <sub>4</sub> to 2 MSO <sub>4</sub> .	·25 MSO <sub>4</sub> to ·5 MSO <sub>4</sub> .
Maximum .....	1·49	3·65	12·5
Minimum .....	·07	·32	·32
Average .....	·69	2·13	5·45
Amalgamated Zinc Plates.			
Maximum .....	·11	·15	1·55
Minimum .....	·01	·02	·01
Average .....	·07	·09	·69
Bright Copper Plates.			
Maximum .....	.....	3·15	2·6
Minimum .....	.....	·65	·48
Average .....	.....	1·95	1·53
Recently coated Electro-copper Plates.			
Maximum .....	.....	·66	·22
Minimum .....	.....	·03	·03
Average .....	.....	·21	·14
Amalgamated Copper Plates.			
Maximum .....	.....	·54	1·4
Minimum .....	.....	·08	·27
Average .....	.....	·28	1·0

As a general rule the weaker the solution the greater is the average difference of potential set up between two plates, as alike as practicable, immersed in the same fluid: *ceteris paribus*, bright plates show much wider limits of variation than amalgamated or electro plates.

It being impossible to ensure equality of surface-conditions

by simply taking pains to make plates as alike as practicable, an approximation to the value that would have been obtained, had the plates been equal in surface-conditions, was arrived at in each experiment by the simple device of exchanging the plates after one series of readings had been taken, and taking another series of readings, averaging the two mean values thus obtained. In many cases the plates were exchanged twice more, and the general mean of all four sets of readings taken. To prevent alteration of solution-strength, the plates exchanged were always rinsed with the solution into which they were about to be dipped before immersion therein. Operating in this way, the difference between the values obtained before and after exchanging represents *double* the sum of the potential difference that would be set up between the plates when opposed to one another in the same solutions respectively. It is noteworthy that the figures thus got by exchanging plates are of the same order of magnitude as those resulting from the opposition of two plates of the same kind. Thus in the above-described experiments the maximum variation observed with amalgamated zinc plates is 1.55 millivolt, and that with electro-copper plates .66 millivolt, giving a sum of 2.21; whilst the corresponding average values give a sum of less than .5 millivolt. With two opposed Daniells set up with amalgamated zinc and electro-copper plates, the halves of the differences observed on exchanging plates averaged less than .5 millivolt, sometimes, however, amounting to 1.0, and occasionally, but only rarely, to 2.0 millivolts; and similarly in other cases.

150. In order to eliminate errors arising from depreciation of E.M.F. through non-adjuvancy, arising from the current-density being greater than the limiting-density below which such effects are inappreciable ("polarization"), several series of observations were made in order to find out what the limiting-densities are for different kinds of plates and fluids, such that the depreciation in E.M.F. shall not exceed a definite small quantity, say .1 to .2 millivolt. The experiments already published made with single Daniell and other analogous cells (§§ 103-105, Part V.) show that with current-densities of from 10 to 20 microamperes per square centimetre of plate-surface (both plates being equal in area, and

one only being reckoned), diminutions in E.M.F. of from 1 to 6 millivolts may be brought about, quantities in many cases far exceeding the potential-differences due to varying solution-strength to be measured. Manifestly, therefore, only very minute currents can be employed when two Daniell or other analogous cells are opposed, and consequently the effect of "polarization" about doubled. Similarly the experiments described in Part IV. (§ 93) indicate that when a current passes between two zinc plates in zinc-sulphate solution, or between two copper plates in copper-sulphate solution, a "counter electromotive force" of a considerable number of millivolts, and even some centivolts, may be set up with current-densities of but a few microamperes per square centimetre; so that in a "diffusion-cell" serious diminutions in the potential-difference actually set up may be brought about by very small current-densities.

In order to determine these limiting current-densities, experiments were made in the following way. The diffusion-cell, or pair of opposed Daniell or other cells to be examined, was set up, as was also a normal Daniell cell for comparison, and the currents from each alternately sent through a large external resistance (using appropriate shunts), series of readings being taken in each case. The resistance was now altered, and two fresh series of readings taken; after which it was again altered, and two more series taken, and so on: usually the whole set of series of readings was repeated in reverse order. The average scale-readings for a series of given total resistances in circuit were thus known both for the Daniell cell and the other one compared with it. With the former, the product of average scale-reading and total resistance was sensibly constant for current-densities that caused an appreciable falling-off in the product similarly obtained with diffusion-cells or with two opposed Daniell cells, &c., showing that whilst "polarization" did not occur to a measurable extent in the first case, it did in the second. The following illustration will make the point clear: two series of readings with varying resistances were made in reverse order with a normal Daniell cell, and with two opposed cells jointly giving an effective E.M.F. of a little more than one-hundredth of that of the Daniell cell; for the

former the  $\tau_{000}^1$  shunt was used, and for the latter the  $\tau_0^1$  shunt.

### Single Daniell Cell.

Total resistance in circuit, in ohms.	Scale-readings.			Product of mean scale-reading into resistance.
	First series.	Reversed series.	Mean.	
200,050	63.7	63.9	63.8	$12.763 \times 10^6$
150,050	84.8	85.3	85.05	$12.762 \times 10^6$
100,050	127.5	127.6	127.55	$12.761 \times 10^6$

Here the product of scale-reading into resistance being constant within the limits of observational error, it is evident that the E.M.F. of the cell was constant within about  $\frac{1}{2000}$  part of its value, notwithstanding that the current rose from  $\frac{1.11}{200050}$  ampere (5.5 microamperes) to  $\frac{1.11}{100050}$  ampere (11.1 microamperes), representing a rise in density of from 2 to 4 microamperes per square centimetre, the plates exposing a surface of about 3 square centimetres each. Each scale-division here represented  $\frac{1.115}{1000 \times 12.762 \times 10^6}$  ampere, or 87.37 classoamperes.

### Two opposed Cells.

Total resistance, in ohms.	Scale-readings.			Current, in microamperes.	E.M.F. in millivolts.	Fall in E.M.F.
	First series.	Reversed series.	Mean.			
200,820	69.3	70.1	69.7	.060897	12.23	—
150,820	92.1	93.25	92.67	.080965	12.21	.02
100,820	137.0	138.0	137.5	.120134	12.11	.11

Hence with an increase of current from .06 to .08 microampere, representing an increase in density from .02 to .027, the fall in E.M.F. was barely measurable, being only .02 millivolt; but when the current rose to .12 microampere, giving a density of .04, the fall in E.M.F. was distinct, being upwards of .1 millivolt.

151. In the same kind of way various other observations were made, and indicated on the whole that the effect of polarization in cells set up with amalgamated-zinc and electro-

copper plates is not greater than about  $\cdot 2$  millivolt, as long as the current-density does not exceed about  $\cdot 05$  microampere per square centimetre of plate-surface.

Limiting values not far from this were similarly obtained with other kinds of zinc- and copper-plate surfaces. Accordingly in the observations made with these kinds of cells for the purpose of estimating the variations in E.M.F. due to difference in solution-strength, the current-densities were never allowed to exceed this limit, and were usually a long way below it.

In precisely the same kind of way the limiting values for various kinds of diffusion-cells were arrived at. The following table represents some of the average results obtained, the E.M.F.'s being expressed in millivolts:—

Current-density, microamperes per square centimetre.	Two opposed Daniell cells.	Diffusion-cells.		
	Amalgamated zinc and electro-copper plates.	Zinc sulphate.		Copper sulphate.
		Electro- zinc plates.	Amalgamated- zinc plates.	Electro- copper plates
Not exceeding $\cdot 02$	Below $0\cdot 02$	Below $\cdot 03$	Inappreciable	Inappreciable
$\cdot 02$ to $\cdot 035$	" $0\cdot 1$	" $\cdot 1$	Below $\cdot 1$	Below $\cdot 1$
$\cdot 035$ " $\cdot 06$	$\cdot 1$ to $\cdot 3$	$\cdot 1$ to $\cdot 2$		
$\cdot 06$ " $\cdot 10$	$\cdot 3$ " $\cdot 5$	$\cdot 2$ " $\cdot 5$	$\cdot 1$ to $\cdot 2$ $\cdot 2$ " $\cdot 4$ $\cdot 4$ " $1\cdot 0$ $1\cdot 0$ " $2\cdot 0$	$0\cdot 1$ to $\cdot 3$
$\cdot 10$ " $\cdot 15$	$\cdot 5$ " $\cdot 8$	$\cdot 5$ " $1\cdot 0$		$\cdot 3$ " $\cdot 5$
$\cdot 15$ " $\cdot 2$	$\cdot 8$ " $1\cdot 2$			$\cdot 5$ " $\cdot 8$
$\cdot 2$ " $\cdot 5$				$\cdot 8$ " $2\cdot 0$
$\cdot 5$ " $\cdot 8$				

It is here noticeable that the amounts of depreciation for given increments in current-density observed with two opposed Daniell cells containing amalgamated-zinc and electro-copper plates are fairly close to the sums of those similarly observed for two diffusion-cells, one containing amalgamated-zinc and the other electro-copper plates. The chemical action in two opposed Daniell cells amounts to solution of copper in one cell and deposition thereof in the other, and ditto for zinc; or precisely the sum of the actions with two diffusion-cells.

The amount of depreciation for a given current-density increase varies notably with the metal and character of surface: thus amalgamated zinc gives less depreciation than electro-copper, and electro-copper less than electro-zinc. Variation in the strength of the solution used did not appear to influ-

ence the result to anything like so great an extent as variation in the nature of the plate-surfaces.

On the whole it was found, even in those cases where the maximum amount of depreciation was produced, that this depreciation did not exceed from  $\cdot 1$  to  $\cdot 2$  millivolt, until the current-density overpassed  $\cdot 02$  to  $\cdot 03$  microampere per square centimetre. In the four cases above cited the limiting current-densities, when the depreciation amounts to  $\cdot 2$  millivolt, are:—

Two opposed Daniell cells, amalgamated-zinc and electro-copper plates .....	$\cdot 05$
Diffusion-cells, electro-zinc plates .....	$\cdot 06$
„ „ amalgamated-zinc plates .....	$\cdot 15$
„ „ electro-copper plates .....	$\cdot 08$

In carrying out the observations, therefore, care was taken\* that in no case should the current-density exceed the limiting value for the particular class of cell examined, current-densities of much less amount being in most cases employed; so that, finally, *the effect of "polarization" on the average values obtained is in no case to depreciate them by a quantity so great as  $\cdot 2$  millivolt, and is usually insufficient to depreciate by an amount approaching to  $\cdot 1$  millivolt.*

152. As a general rule, it was found that when the cell (or pair of opposed cells) to be examined was set up, comparatively little variation in the current flowing took place during 15 to 30 minutes; what alteration did occur being evidently due to alteration in condition of plate-surface (by superficial oxidation by dissolved air, or by molecular change, *i. e.* spontaneous change of state of aggregation, or by solution or deposition of external film as the current flowed producing electrolysis), and being only a fraction of the variation produced on exchanging plates. With bright zinc plates, however, the alteration during a few minutes after setting up was

\* Owing probably to the influence of "polarization," the values obtained by Fromme, *loc. cit. supra*, do not exhibit very close concordance with one another, nor do the mean curves thence deducible agree sharply with those subsequently detailed. Moser's diffusion-cell figures, on the other hand, do not differ widely from those obtained by us.

often considerable and irregular in direction. The numbers given in the subsequent section are in all cases deduced from the average readings of the cells during the first 15 or 20 minutes after first setting up, or after exchanging plates, as the case might be; the mean of the two averages thus obtained (or of the four, if three exchanges were made after taking the first set of readings) being finally adopted as the mean value for the particular experiment.

As regards the experiments with the diffusion-cells, these were ordinarily constructed of two beakers united by an inverted Y-shaped tube, the ends of which were covered with bladder or other thin membrane, and filled with either of the two solutions used, one in one beaker, the other in the other: in short, they were precisely similar to the forms of Raoult cell used in the preceding portions of these researches. It was thought desirable to see if any influence could be traced as exerted by the membranes as such, and accordingly a number of gravity diffusion-cells were set up by pouring into a long U-tube the stronger of the two solutions used until rather more than half full, and then very cautiously running slowly into one limb the weaker solution, so as to have a well-marked line of demarcation between the two fluids. Two plates were then immersed in the two solutions and exchanged after taking readings, and so on. Both with zinc sulphate and copper sulphate no measurable differences could be detected between the average results obtained with these cells and with the Raoult form of cell, both sets of cells having respectively the same fluids and kinds of plates; clearly proving that the membranes as such exercised no measurable influence on the results.

As an illustration of the general character of the experiments made, the following observations with two opposed Daniell cells may be cited as an example, typical in all respects saving, first, that the values obtained before and after exchanging plates differ more than usual (for which reason this experiment is selected); and, secondly, that the galvanometer was regulated so as to be considerably less sensitive than was found desirable for other experiments, on account of the comparatively large potential-difference to be measured.

Plates used : amalgamated zinc and electro-copper.

Solutions used : per 100  $\text{H}_2\text{O}$ , 2.0  $\text{CuSO}_4$  throughout ; 5.584  $\text{ZnSO}_4$  in one cell and .1012  $\text{ZnSO}_4$  in the other.

Valuation of scale : a normal Daniell cell (set up with amalgamated zinc, electro-copper, and zinc- and copper-sulphate solutions of equal strength) gave 125.7 scale-degrees as mean reading when 200100 ohms were in circuit, the  $\frac{1}{100}$  shunt being used, whence 1 scale-division =  $\frac{1.114}{100 \times 200100 \times 125.7}$  ampere = .000443 microampere = 443 classoamperes.

Readings before exchanging plates.	After exchanging plates.
Average scale-reading (no shunt used)..... 484.25	467.0
Current passing, in micro-amperes*..... .2145	.2069
Total resistance in circuit, in ohms ..... 207400	207400
E.M.F., in millivolts ..... 44.5	42.9
Mean of the two results ..... 43.7 millivolts.	
Maximum departure between ditto . 1.6 millivolt.	
Difference from mean ..... $\pm .8$ „	

In the same kind of way other similar experiments gave means ranging from 41.6 to 44.4 millivolts, the final average being 43.3, with a probable error of  $\pm .34$  millivolt.

153. The following tables give, in millivolts, the results obtained with various kinds of metals, natures of plate-surfaces, and descriptions of saline solutions :—

#### I. *Variations of Potential due to Variations of Strength in Zinc-sulphate Solution.*

##### 1. *Amalgamated Zinc Plates.*

##### A. Observations with the Electrometer.

Probable error of each value cited not exceeding  $\pm 1.0$  millivolt. The numbers represent the difference of potential set up when one solution is  $m \text{ ZnSO}_4 100 \text{ H}_2\text{O}$ , and the other  $n \text{ ZnSO}_4 100 \text{ H}_2\text{O}$ .

\* Representing a current-density of about .045 microampere per square centimetre.

Value of $m$ .	Value of $n$ .					
	4.2	3.0	2.1	1.1	.55	.167
5.1	4	12	16	23	28	37
4.2	.....	8	12	19	24	33
3.0	.....	.....	4	11	16	25
2.1	.....	.....	.....	7	12	21
1.1	.....	.....	.....	.....	5	14
.55	.....	.....	.....	.....	.....	9

B. With two opposed Daniell cells, the copper plates being united and the zinc plates the terminal ones, the following values were obtained. The probable error of each value cited is less than in the electrometer-experiments, being usually well within  $\pm .5$  millivolt, often no more than  $\pm .25$  millivolt

Value of $m$ .	Value of $n$ .					
	3.995	3.005	2.158	1.016	.497	.1012
5.584	10.5	16.1	20.2	26.7	32.3	43.3
3.995	.....	5.6	9.7	16.2	21.8	32.8
3.005	.....	.....	4.1	10.6	16.2	27.2
2.158	.....	.....	.....	6.5	12.1	23.1
1.016	.....	.....	.....	.....	5.6	16.6
.497	.....	.....	.....	.....	.....	11.0

C. With Diffusion-cells the following values were obtained: probable error of each value less than  $\pm .5$  millivolt:—

Value of $m$ .	Value of $n$ .					
	3.95	3.10	2.00	.96	.50	.237
5.25	6.8	12.4	18.4	24.7	29.2	35.0
3.95	.....	5.6	11.6	17.9	22.4	28.2
3.10	.....	.....	6.0	12.3	16.8	22.6
2.00	.....	.....	.....	6.3	10.8	16.6
.96	.....	.....	.....	.....	4.5	10.3
.50	.....	.....	.....	.....	.....	5.8

On graphical representation all three sets of figures are found to accord fairly well when, by interpolation, the figures are all reduced to a common origin for the three curves, viz. when  $m=5.0$ . The following table gives the result thus reduced to common origin and the same abscissæ.

	Electrometer.	Two opposed cells.	Diffusion-cells.	Average.
5.584	.....	- 3.8		
5.25	.....	.....	- 1.3	
5.1	- 0.4	.....	.....	
5.0	0	0	0	0
4.0	4.8	6.7	5.2	5.6
3.0	11.6	12.3	11.6	11.8
2.0	16.3	17.3	17.1	16.9
1.0	23.5	23.1	23.1	23.2
.5	28.7	28.5	27.9	28.4
.237	34.9	35.7	33.7	34.8
.167	36.6	37.7	.....	37.2
.100	.....	39.5	.....	39.5

It is evident that, having regard to the impossibility of completely eliminating errors from difference of character of plate-surface, these numbers coincide sufficiently closely to show that whether no current at all circulates (electrometer), or a small current not too great to set up any notable "polarization," *sensibly the same numbers result whether the observations be made by carefully valuing separate cells and subtracting the values from one another; by opposing two cells and measuring the current due to the difference in their E.M.F.'s; or by means of diffusion-cells* (representing the terminal liquids of two opposed cells of Raoult's form, when directly connected). The same conclusions also follow from the observations detailed in § 154 made with copper-sulphate solution and electro-copper plates.

## 2. Electro-zinc Plates.

Observations made with Diffusion-cells only: probable error-in no case exceeding  $\pm 0.75$  millivolt.

	$n=3.005$	$n=1.016$	$n=.1012$
$m=5.584$	11.2	20.0	30.5
3.005	.....	8.8	19.3
1.016	.....	.....	10.5

## 3. Bright Zinc Plates.

Observations with Diffusion-cells only: very much less concordance between the results of these experiments than with other kinds of zinc plates, and much more alteration (and of more irregular character) on allowing cells to stand a few minutes.

Probable error about  $\pm 1.5$  millivolt.

	$n=3.005$	$n=1012$
$m=5.584$	10.0	29.6
$=3.005$	.....	19.6

The following table represents these three sets of values reduced by interpolation to a common origin ( $m=5.0$ ) and common abscissæ: the curves respectively marked 1, 2, and 3 in fig. 1, Plate V., indicate the three sets of reduced values thus obtained.

Difference of Potential set up between Solutions of  $5.0 \text{ ZnSO}_4$   
 $100 \text{ H}_2\text{O}$  and  $n \text{ ZnSO}_4$   $100 \text{ H}_2\text{O}$ .

	Amalgamated zinc (average above cited)	Electro- zinc.	Bright zinc.
$n=5.0$	0	0	0
$=3.0$	11.8	8.6	7.7
$=1.0$	23.2	17.5	15.8
$=0.1$	39.5	27.9	25.3

Evidently the values with amalgamated zinc are the highest, and those with bright zinc the lowest.

#### 154. II. *Variations of Potential due to Variation in Strength of Copper-sulphate Solution.*

##### 1. *Electro-copper Plates.*

A. Observations with the Electrometer. Probable error not exceeding  $\pm 1$  millivolt.

Values of $m$ .	Values of $n$ .		
	1.10	.55	.167
2.1	5	11	20.5
1.1	.....	6	13.5
.55	.....	.....	9.5

B. With two Opposed Cells. Probable error usually well within  $\pm .5$  millivolt, and often less than  $\pm .25$  millivolt.

	$n=.940$	$n=.461$	$n=.094$
$m=1.972$	5.6	10.3	22.4
$=.940$	.....	4.7	16.8
$=.461$	.....	.....	12.1

C. With Diffusion-cells. Probable error less than  $\pm 0.5$  millivolt.

	$n=0.99$	$n=0.47$	$n=0.227$
$m=1.88$	5.7	10.5	16.3
$=0.99$	.....	4.8	10.6
$=0.47$	.....	.....	4.7

On graphical representation after reduction, by interpolation, to common origin (when  $m=2.0$ ) and common abscissæ, these three sets of figures are found to coincide within reasonable error-limits, thus confirming the results arrived at above with amalgamated-zinc plates and zinc-sulphate solutions. Further, it is noticeable that these values are all close to those similarly obtained with zinc-sulphate solutions and amalgamated-zinc plates when similarly reduced.

Value of $m$ .	Electro-meter.	Two opposed cells.	Diffusion-cells.	Average.	Average with zinc sulphate and amalgamated-zinc plates.
2.1	-5	.....	.....	.....	.....
2.0	0	0	0	0	0
1.972	.....	2	.....	.....	.....
1.88	.....	.....	8	.....	.....
1.0	5.6	5.5	6.4	5.8	6.3
.5	11.7	10.1	11.0	10.9	11.5
.227	18.5	18.2	17.1	17.9	18.2
.167	20.0	20.2	.....	20.1	20.3
.100	21.7	22.4	.....	22.0	22.6
.094	21.8	22.6	.....	.....	.....

It would hence result that the E.M.F. of a Daniell cell set up with zinc- and copper-sulphate solutions *of the same molecular strength*, and amalgamated-zinc and electro-copper plates, cannot exhibit any very marked variation, whatever the actual strength of the solutions, inasmuch as whatever effect on the E.M.F. is produced by a given variation in the strength of the zinc-sulphate solution must be very nearly counterbalanced by the equal and opposite effect of the same variation in the strength of the copper-sulphate solution. If, however, electro-zinc or bright zinc plates be used, the E.M.F. must rise with the strength of the solutions, the copper-sulphate variation effect overpowering the zinc-sulphate variation effect. In other words, if  $e$  be the E.M.F. of the cell for a

given low strength of solution, and  $E$  that for a greater strength, then  $E = e + a - b$  (§ 148): with amalgamated zinc and electro-copper plates,  $a$  nearly  $= b$ ; but with electro or bright zinc,  $a < b$ .

The following experiments show that the value of  $a$ , *cæteris paribus*, is greater with amalgamated, but less with bright, than with electro copper; so that with cells set up with amalgamated zinc plates, the value of the E.M.F. rises with the strength of the solutions when amalgamated copper plates are opposed, and falls when bright copper plates are used instead.

## 2. Amalgamated Copper Plates.

Observations with Diffusion-cells. Probable error not exceeding  $\pm 0.75$  millivolt.

	$n = .940$	$n = .461$	$n = .094$
$m = 1.972$	6.0	12.0	27.5
.940	.....	6.0	21.5
.461	.....	.....	15.5

## 3. Bright Copper Plates partially but not completely Electro-coated.

Observations with Diffusion-cells. Probable error not exceeding  $\pm 0.75$  millivolt.

	$n = .940$	$n = .461$	$n = .094$
$m = 1.972$	4.1	9.3	19.7
.940	.....	5.2	15.6
.461	.....	.....	10.4

## 4. Bright Copper Plates.

Observations with Diffusion-cells. Probable error not exceeding  $\pm 1.0$  millivolt.

	$n = .461$	$n = .094$
$m = 1.972$	6.9	16.8
.461	.....	9.9

The following table represents these four sets of values reduced, by interpolation, to a common origin ( $m = 2.0$ ) and common abscissæ: the curves marked respectively 1, 2, 3, and 4, fig. 2, represent these sets of reduced values: curve 5 similarly represents the average values for amalgamated zinc and

zinc-sulphate solution similarly reduced; evidently nearly coinciding with curve 2 (electro-copper).

Difference of Potential set up between Solutions of  $2.0 \text{ CuSO}_4$   
 $100 \text{ H}_2\text{O}$  and  $n\text{CuSO}_4$   $100\text{H}_2\text{O}$ .

	Amalgamated copper.	Electro- copper.	Bright copper only partially electro-coated.	Bright copper.
$n=2.0$	0	0	0	0
$=1.0$	5.9	5.8	4.0	3.5
$=.5$	11.7	10.9	9.0	6.6
$=.1$	27.2	22.0	19.6	16.8

155. A number of observations were similarly made with various cadmium-sulphate solutions, employing different kinds of cadmium plates: only diffusion-cells were used in this series of experiments. The following results were obtained as final average values, showing that amalgamated plates (wet with liquid amalgam) give higher, and bright plates lower values than electro-coated plates, just as with zinc and copper.

1. *Electro-cadmium Plates*.—Probable error of each value less than  $\pm .5$  millivolt.

Value of $m$ .	Value of $n$ .					
	4.95	3.205	2.01	1.02	.46	.235
6.10	6.0	14.2	19.5	24.7	29.9	34.2
4.95	.....	8.2	13.5	18.7	23.9	28.2
3.205	.....	.....	5.3	10.5	15.7	20.0
2.01	.....	.....	.....	5.2	10.4	14.7
1.02	.....	.....	.....	.....	5.2	9.5
.46	.....	.....	.....	.....	.....	4.3

2. *Bright Cadmium Plates*.—Probable error less than  $\pm .75$  millivolt.

Value of $m$ .	Value of $n$ .					
	4.95	3.205	2.01	1.02	.46	.235
6.10	4.9	13.7	18.5	23.0	27.4	30.5
4.95	.....	8.8	13.6	18.1	22.5	25.6
3.205	.....	.....	4.8	9.3	13.7	16.8
2.01	.....	.....	.....	4.5	8.9	12.0
1.02	.....	.....	.....	.....	4.4	7.5
.46	.....	.....	.....	.....	.....	3.1

3. *Amalgamated Cadmium*.—Surface wet with fluid amalgam. Probable error not exceeding  $\pm 0.75$  millivolt.

	$n=2.01.$	$n=1.02.$	$n=.235.$
$m=6.10.....$	20.6	26.3	35.9
$=2.01.....$	.....	5.7	15.3
$=1.02.....$	.....	.....	9.6

4. *Amalgamated Cadmium*.—Surface not fluid, but crystalline. Probable error not exceeding  $\pm 1.5$  millivolt.

	$n=2.01.$	$n=1.02.$	$n=.235.$
$m=6.10$	14.5	19.6	24.5
$=2.01$	.....	5.1	10.0
$=1.02$	.....	.....	4.9

The following tables are obtained from the above values by interpolation, as in the above observations with zinc and copper sulphates:—

Difference of Potential set up between Solutions of  $5.0 \text{ CdSO}_4$   
 $100 \text{ H}_2\text{O}$  and  $n \text{ CdSO}_4$   $100 \text{ H}_2\text{O}$ .

	Amalgamated cadmium, fluid.	Electro- cadmium.	Bright cadmium.	Amalgamated cadmium, crystalline.
$n=5.0.....$	0	0	0	0
$3.0.....$	10.1	9.9	10.5	7.1
$2.0.....$	15.1	13.9	13.8	10.6
$1.0.....$	20.9	19.2	18.4	15.8
$0.5.....$	25.6	23.8	22.4	18.3
$0.235.....$	30.4	28.5	25.8	20.6

Difference of Potential set up between Solutions of  $2.0 \text{ CdSO}_4$   
 $100 \text{ H}_2\text{O}$  and  $n \text{ CdSO}_4$   $100 \text{ H}_2\text{O}$ .

	Amalgamated cadmium, fluid.	Electro- cadmium.	Bright cadmium.	Amalgamated cadmium, crystalline.
$n=2.0.....$	0	0	0	0
$=1.0.....$	5.8	5.3	4.6	5.2
$=.5.....$	10.5	9.9	8.6	7.7
$=.235.....$	15.3	14.6	12.0	10.6

Curves 1 to 4 (figs. 3 and 4) represent these sets of values respectively: it is noticeable that the curve obtained with crystalline amalgam plate-surfaces underlies the others.

On contrasting the first of these tables with that similarly obtained with zinc sulphate (§ 153), and the second with that obtained with copper sulphate (§ 154), it is evident that with



On reducing these two sets of figures to the values for  $m=10$  as origin, and plotting the resulting numbers, the curves marked 1 and 2 respectively (Pl.V. fig. 5) are obtained: evidently the value of  $b$  in the expression  $E=e+a-b$  greatly exceeds that of  $a$  for all cases where equal molecular strengths of solutions are used in zinc-cadmium-chloride cells; *i. e.* the E.M.F. of a cell set up with zinc and cadmium chlorides, amalgamated zinc, and electro-cadmium decreases as the solution-strength increases, both solutions being equal in strength.

A number of observations made with the galvanometer showed that this is the case, and that the value of the E.M.F. of any zinc-cadmium-chloride cell is given in volts by the equation

$$E = \cdot 330 + a - b,$$

where  $\cdot 330$  is the E.M.F. of a cell containing amalgamated-zinc and electro-cadmium plates, and solutions of the chlorides of equal strength  $\cdot 25 \text{ MCl}_2 \text{ } 100 \text{ H}_2\text{O}$ ; whilst  $a$  and  $b$  are the values deduced from the above tables for the difference of potential set up for solutions of this strength as compared with the particular strengths employed in the cell examined.

157. A noteworthy point in connexion with the value  $\cdot 330$  volt for solutions  $\cdot 25 \text{ MCl}_2 \text{ } 100 \text{ H}_2\text{O}$  is the following. According to Julius Thomsen (*Journ. Prakt. Chemie*, xi. p. 402), the heats of formation of cadmium and zinc sulphates dissolved in  $400 \text{ H}_2\text{O}$  ( $\cdot 25 \text{ MSO}_4 \text{ } 100 \text{ H}_2\text{O}$ ) exhibit exactly the same difference as exists between those of cadmium and zinc chlorides dissolved in  $200 \text{ H}_2\text{O}$ ; thus:—

Zn, O, SO <sub>3</sub> , aq = 106090	Zn, Cl <sub>2</sub> , aq = 112840
Cd, O, SO <sub>3</sub> , aq    89500	Cd, Cl <sub>2</sub> , aq    96250
— 16590	— 16590

Consequently, as the heat of dilution of  $\text{ZnCl}_2 \text{ } 200 \text{ H}_2\text{O}$  to  $\text{ZnCl}_2 \text{ } 400 \text{ H}_2\text{O}$  exceeds that of  $\text{CdCl}_2 \text{ } 200 \text{ H}_2\text{O}$  to  $\text{CdCl}_2 \text{ } 400 \text{ H}_2\text{O}$ , and the excess is to be added to the above difference in the case of the chlorides, the heat evolved in the displacement of cadmium by zinc from  $\text{CdCl}_2 \text{ } 400 \text{ H}_2\text{O}$  is slightly *greater* than that from  $\text{CdSO}_4 \text{ } 400 \text{ H}_2\text{O}$ . The electromotive forces of zinc-cadmium-sulphate and zinc-cadmium-chloride cells for solutions of strengths  $\text{MSO}_4 \text{ } 400 \text{ H}_2\text{O}$ , and  $\text{MCl}_2 \text{ } 400 \text{ H}_2\text{O}$  ( $\cdot 25 \text{ MSO}_4$  and  $\cdot 25 \text{ MCl}_2$  per  $100 \text{ H}_2\text{O}$ ) do not ex-

hibit this relationship: on the contrary, the E.M.F. of the latter is materially *less* than that of the former; and, further, is distinctly less than that corresponding to the heat evolved in the net chemical change with which the E.M.F. of the former fairly coincides; thus:—

E.M.F. corresponding to 16590 gramme-degrees per gramme-molecule, or 8295 per gramme equivalent .....	} = .365 volt.
Observed E.M.F. with zinc-cadmium-sulphate cells set up with solutions of .25 MSO <sub>4</sub> , 100 H <sub>2</sub> O, amalgamated-zinc and electro-cadmium plates (§ 121, Part VI.) .....	
Observed E.M.F. with zinc-cadmium-chloride cells set up with solutions of .25 MCl <sub>2</sub> , 100 H <sub>2</sub> O, amalgamated-zinc and electro-cadmium plates.....	} = .330 "

The difference between .365 and .330 volt, or .035 volt, represents nearly 10 per cent. of the former value, and corresponds to upwards of 1500 gramme-degrees per gramme molecule, a quantity almost too large to be likely to be due solely to accumulation of experimental errors. This point will be further discussed in a future paper.

158. No material difference is made in the relationships between the E.M.F.'s observed (deduced from the assumption that the E.M.F. of Clark's cell = 1.457 volt) and those calculated from the heat-values (by using the factor 4410), when, instead of the numerical values 1.457 and 4410 for these quantities (hitherto purposely employed throughout for the sake of uniformity), the more exact values are used deduced from more recent observations on the true value of the B.A. unit of resistance, and especially those of Lord Rayleigh, which indicate that the true value is only  $.9868 \times 10^9$ . For the use of this corrected value reconciles the apparent discrepancy between Joule's various valuations of the mechanical equivalent of heat (§§ 33, 34, Part I.); and, further, causes all the different estimations of the value of J discussed in §§ 55 and 56 (Part III.) to agree fairly well together, and to become on reduction values close to the mean result of Joule's friction

experiments, viz.  $41\cdot555$  megalergs (§ 34). Combining this value of  $J$  with the mean value of the "Faraday coefficient" (the quantity referred to in § 7, Part I., as indicated by  $\chi$ , but which may be gracefully indicated instead by  $F$  in commemoration of Faraday) deducible from the experiments of Kohlrausch and the more recent ones of Mascart, viz.  $\cdot0001048$  (§ 103, footnote, Part V.), the end result is attained that

$$JF = 41\cdot555 \times 10^6 \times \cdot0001048 = 4355.$$

Now  $4355 = 4410 \times \cdot9875$ ; so that whilst the actual measurements of E.M.F. are reduced in the ratio  $\cdot9868$ , those deduced from heat-valuations must concurrently be reduced in the ratio  $\cdot9875$ , or almost exactly to the same extent. If  $J$  be taken  $= 41\cdot5 \times 10^6$ , the reduction ratio becomes  $\cdot9862$  instead of  $\cdot9875$ . Hence it appears that in order to reduce to the values most consistent with the bulk of evidence at present extant the various E.M.F. determinations described in the previous portions of these researches, it will practically suffice to multiply them by  $\cdot987$ , *i. e.* to subtract  $1\cdot3$  per cent. of their value, whether the figures be direct determinations of E.M.F. or deductions from calorimetric experiments.

It may further be noticed that when the value  $\cdot987 \times 10^9$  for the B.A. unit is taken, in consequence that of Clark's cell becomes  $\cdot987 \times 1\cdot457 = 1\cdot438$  volt; so that the mean value of the E.M.F. corresponding to the work done in electrolysing water, as directly determined in Part II. § 46, becomes  $1\cdot4808 \times 10^8$  C.G.S. units, taking  $J = 41\cdot555 \times 10^6$  instead of  $42 \times 10^6$ , as in Part II. The mean heat-valuation arrived at § 31, Part I., from the results of various experimenters employing the calorimeter, being 34100 gramme-degrees, the product  $34100 \times JF$  becomes  $34100 \times 4355 = 1\cdot4850$ , which value exceeds  $1\cdot4808$  by only  $\cdot29$  per cent., a quantity falling within the limits of probable error in the experiments ( $\pm \cdot32$  per cent.). Inasmuch as from various causes a slight systematic error of defect necessarily attended the direct determinations, the final conclusion is warranted that these direct determinations are sensibly in accordance with the two propositions, firstly that the B.A. unit is actually only  $\cdot987 \times 10^9$ ; and, secondly, that Clark's cell has an E.M.F. of  $\cdot987 \times 1\cdot457 = 1\cdot438$  volt.

159. The experiments described in §§ 153 and 154 lead to the conclusion that a Daniell cell containing solutions of zinc and copper sulphate of equal strengths has an almost invariable E.M.F. whatever the strengths of the solutions when the plates are of amalgamated zinc and electro-copper; but rises in E.M.F. if the plates are either amalgamated zinc and amalgamated copper, electro-zinc and electro-copper, or, *à fortiori*, electro-zinc and amalgamated copper. It seemed desirable to substantiate these deductions more rigorously. Accordingly two pairs of solutions of zinc and copper sulphate were carefully prepared, such that one pair had the composition  $2.069 \text{ MSO}_4 \cdot 100 \text{ H}_2\text{O}$ , and the other the composition  $.0937 \text{ MSO}_4 \cdot 100 \text{ H}_2\text{O}$ . Cells were then set up with these fluids, opposed to one another, and series of readings taken. It was found that the numbers thus obtained exhibited much greater divergences and fluctuations than those similarly obtained with cells where the molecular strengths of the solutions were not equal in each case respectively. In the latter case the current always passed in one direction, and did not exhibit any very marked alteration in magnitude during the first 15 to 30 minutes after setting up (during which period the observations above described were ordinarily made); but with two opposed Daniell cells, containing pairs of solutions of the same strengths in each severally, the differential current sometimes passed in one direction on first setting up, sometimes in the opposite direction; sometimes it increased in intensity as time elapsed, and sometimes it diminished: in the latter case occasionally it diminished to *nil*, and then flowed in the opposite direction with gradually increasing intensity. Thus, for instance, the following numbers were obtained in one set of observations where the density never exceeded .02 microamperes per square centimetre, and was usually much less, so that "polarization" errors were eliminated (§ 150). The total resistance in circuit (including galvanometer and cells) was 107,400 B.A. units. The sign + indicates that the E.M.F. of the cell containing the stronger solutions was higher than that of the other; the sign - indicates the opposite. Readings were taken every minute for 15 minutes after setting up; the plates were then exchanged (after rinsing with the appropriate solutions), and another similar series of readings taken: a

second, and then a third exchange was similarly made, readings for 15 minutes being again taken in each case: the readings are translated into millivolts, every scale-division being equal, in these experiments, to  $85.7 \text{ elassoamperes}$ , and consequently representing  $85.7 \times 10^{-12} + 107,400 = .00000895 \text{ volt} \approx 8.95 \text{ microvolts}$ .

Minutes after first setting up.	Before plates exchanged.	After first exchange.	After second exchange.	After third exchange.
1 .....	-1.3	-2.0	+4.5	+5.4
2 .....	-1.4	-2.0	+3.2	+3.4
3 .....	-1.5	-2.1	+2.1	+2.0
4 .....	-1.5	-2.1	+1.3	+1.0
5 .....	-1.5	-2.1	+ .7	+ .5
6 .....	-1.5	-2.2	+ .4	- .7
7 .....	-1.5	-2.2	+ .1	-1.3
8 .....	-1.6	-2.2	- .3	-1.7
9 .....	-1.6	-2.2	- .5	-2.0
10 .....	-1.6	-2.2	- .7	-2.2
11 .....	-1.6	-2.2	- .8	-2.4
12 .....	-1.6	-2.1	- .9	-2.5
13 .....	-1.6	-2.1	-1.0	-2.6
14 .....	-1.6	-2.1	-1.0	-2.7
15 .....	-1.6	-2.1	-1.0	-2.7
Average ...	-1.5	-2.1	+ .4	- .6
General average ..... = -0.9.				

In precisely the same way the following numbers were obtained in a duplicate experiment:—

During 1st minute.	}	-2.3	-1.1	+2.7	+3.4
During 8th minute.		-1.6	- .4	+1.4	+2.2
During 15th minute.		-1.3	- .1	+ .7	+1.2
Average of all observations.	}	-1.6	- .5	+1.5	+2.1
General average ..... = +.4.					

The mean of this and the preceding experiment gives  $-.25$ , an amount evidently quite negligible in comparison with the fluctuations in the value of the net E.M.F. in operation in the several series of observations; and hence indicating that the E.M.F. of a cell set up with zinc- and copper-sulphate solutions of the same strength, amalgamated zinc and electro-copper,

*is really independent of the solution-strength within the limits of observational error.*

Using the same solutions in the same way the following values were obtained, showing that the E.M.F. really does rise perceptibly with the solution-strength when amalgamated copper is substituted for electro-copper, or when electro-zinc is substituted for amalgamated zinc :—

#### Amalgamated Zinc and Amalgamated Copper.

During 1st minute.	}	-·5	+15·3	+9·1	+13·0
During 8th minute.		-·7	+ 7·7	+1·3	+ 5·7
During 15th minute.		-·8	+ 5·2	0	+ 3·8
Average of all observations.	}	-·7	+ 9·0	+2·7	+ 6·5
General average ..... = +4·4.					

#### Electro-zinc and Electro-copper.

During 1st minute.	}	-1·2	+6·3	+8·2	+7·2
During 8th minute.		+0·9	+4·0	+5·7	+4·4
During 15th minute.		+1·8	+2·9	+3·4	+3·5
Average of all observations.	}	+ ·3	+4·2	+5·6	+4·8
General average ..... = +3·7.					

#### Electro-zinc and Amalgamated Copper.

During 1st minute.	}	+5·4	+6·9	+7·8	+11·1
During 8th minute.		+5·4	+5·5	+5·8	+ 8·0
During 15th minute.		+5·5	+4·3	+5·1	+ 5·8
Average of all observations.	}	+5·4	+5·5	+6·1	+ 7·9
General average ..... = +6·2.					

*Heat developed during Intermixture of Solutions of Zinc (Copper or Cadmium) Sulphates or Chlorides of different Strengths.*

160. The results above described show that when two solutions of different strengths, but containing the same metallic salt, are allowed to intermix by diffusion, plates of the metal contained in the salt immersed in the two solutions respectively acquire different potentials, the potential-difference set up with any given pair of solutions being to some extent dependent on the surface-characters of the plates employed, but being, *cæteris paribus*, greater the greater the difference between the strengths of the solutions, the plates immersed in the stronger solution acquiring the higher potential. It is evident that if there is a development of heat during intermixture of the solutions used, the work done by a current developed on connecting the plates by a conductor may reasonably be supposed to be done in virtue of this heat-development, just as the work done by an ordinary voltaic couple is done in virtue of the heat developed by the chemical actions taking place therein. Accordingly it becomes of interest to determine precisely what amounts of heat are actually generated during intermixture in order to see what relationships hold between the electromotive forces actually generated and those corresponding to the heat-developments.

The required "heats of intermixture" are readily calculable from the values representing the "heats of dilution" obtained by measuring the amounts of heat produced when solutions of metallic salts are diluted to known extents by means of water. If  $h_1$ ,  $h_2$ ,  $h_3$  respectively represent the heats of dilution of gramme-molecules of the three solutions  $\text{MSO}_4 \cdot 2a \text{H}_2\text{O}$ ,  $\text{MSO}_4 \cdot 2b \text{H}_2\text{O}$ , and  $\text{MSO}_4 \cdot (a + b) \text{H}_2\text{O}$  to the same further extent, then  $H$ , the heat produced by mixing a gramme-molecule of the first solution with one of the second so as to produce two of the third, is given by the equation

$$H = h_1 + h_2 - 2h_3.$$

In order to obtain the data for the calculation of the various values of  $H$  in the case of the solutions examined in the preceding pages, a number of calorimetric determinations were made, substantially in the way described by Julius Thomsen

(*Thermochemische Untersuchungen*, i. p. 18, 1882), using a calorimeter containing 1 litre of fluid in the lower compartment. The quantity of salt employed was usually close upon  $\frac{1}{2}$  gramme-molecule, the weight being arranged so that the resulting fluid was of the strength  $\text{MSO}_4 \cdot 400 \text{H}_2\text{O}$ , or  $\text{MCl}_2 \cdot 400 \text{H}_2\text{O}$ . The thermometers used were graduated in millimetres, about 11 millimetres representing  $1^\circ \text{C}$ .; so that readings being made to  $\pm \frac{1}{20}$  millim., the thermometer-error was  $\pm \frac{1}{20}$  of  $1^\circ \text{C}$ . As determined by means of various blank experiments (with water only intermixed), the limit of accuracy of each experiment was within  $\pm 10$  gramme-degrees; so that each observation might be erroneous within the limits of not exceeding  $\pm 70$  gramme-degrees per gramme-molecule; but as several observations were usually made and averaged, the probable error of each average was ordinarily within  $\pm 25$  gramme-degrees. The following numbers were ultimately obtained as means from upwards of fifty observations, indicating the heat-evolution, in gramme-degrees per gramme-molecule, on diluting  $m \text{MSO}_4 \cdot 100 \text{H}_2\text{O}$  to  $\cdot 25 \text{MSO}_4 \cdot 100 \text{H}_2\text{O}$ , or  $m \text{MCl}_2 \cdot 100 \text{H}_2\text{O}$  to  $\cdot 25 \text{MCl}_2 \cdot 100 \text{H}_2\text{O}$ . Plate V. fig. 6 represents the values graphically.

	Zinc sulphate.	Copper sulphate.	Cadmium sulphate.	Zinc chloride.	Cadmium chloride.
$m=25$ .....	.....	.....	.....	9000	
20.....	.....	.....	.....	8050	
10.....	.....	.....	.....	6100	
7.....	.....	.....	1450		
6.....	.....	.....	1075		
5.....	375	.....	825	4800	100
4.....	175	.....	625	4400	
3.....	100	.....	450	3800	
2.....	50	50	275	2700	
1.5 } 1 } .5 }	Less than errors of observation.	Less than errors of observation.	200 75 .....	1250 400	

161. On calculating from these figures the values of  $h_1$ ,  $h_2$ , and  $h_3$ , and hence those of  $H$ , for particular cases, it becomes evident that, as a general rule, the E.M.F. corresponding to the value of  $H$  falls below the potential-difference actually set up between two plates immersed in solutions of different strengths, the difference being sometimes very considerable. Thus the following tables represent the results thus calculated

when solutions  $\text{MSO}_4 \cdot 2a\text{H}_2\text{O}$  and  $\text{MSO}_4 \cdot 2b\text{H}_2\text{O}$  are intermixed so as to form  $\text{MSO}_4 \cdot (a+b)\text{H}_2\text{O}$  when  $b=200$ , and consequently when  $h_2=0$ . The "observed" values quoted are those obtained with electro-coated plates throughout, save in the case of zinc chloride, where amalgamated plates were employed; all the electromotive forces are expressed in millivolts.

Zinc Sulphate.							
$2a$ .	$a+b$ .	$h_1$ .	$2h_2$ .	H.	Corresponding E.M.F.	Observed E.M.F.	Excess.
20	210	375	0	375	8	27	19
25	212.5	175	0	175	4	22	18
33.3	216.7	100	0	100	2	17	15
50	225	50	0	50	1	13	12
100	250	0	0	0	0	8	8
Copper Sulphate.							
50	225	50	0	50	1	17	16
100	250	0	0	0	0	12	12
200	300	0	0	0	0	6	6
Cadmium Sulphate.							
16.7	208.3	1075	25	1025	23	34	11
20	210	825	25	775	17	28	11
25	212.5	625	25	575	13	23	10
33.3	216.7	450	25	400	9	18	9
50	225	275	25	225	5	14	9
66.7	233.3	200	25	150	3	9	6
100	250	75	20	35	1	4	3
Zinc Chloride.							
4	202	9000	790	8210	181	264	+83
5	202.5	8050	790	7260	160	225	+65
10	205	6100	780	5320	118	149	+31
20	210	4800	760	4040	89	65	-24
25	212.5	4400	750	3650	80	57	-23
33.3	216.6	3800	730	3070	68	52	-16
50	225	2700	700	2000	44	40	-4
100	250	1250	600	650	14	23	+9
Cadmium Chloride.							
20	210	100	0	100	2	32	30
100	250	0	0	0	0	14	14

Analogous results are obtained when the calculations are similarly made for other kinds of mixture: the observed E.M.F. generally notably exceeds that calculated from the heat of intermixture\*. It would hence seem that the *modus operandi* of a "diffusion-cell" is to some extent rather analogous to that of a thermo-couple than to that of an ordinary galvanic element, part at least of the energy gained outside the battery being due, not to the heat-development during chemical action taking place, but to the transformation of sensible heat into electric-current energy. It is noteworthy, moreover, that analogous phenomena are presented in cases where strong and weak solutions of acids (*e. g.* nitric and sulphuric) interdiffuse, platinum or other unoxidizable plates being employed: diffusion-cells of this kind are now being examined.

By uniting together in series a sufficient number of diffusion-cells, all the effects of an ordinary voltaic battery can be produced, at least those compatible with the presence of a large resistance in circuit: electrolysis of metallic solutions (*e. g.* copper sulphate) is readily brought about.

*Volume-alteration on Intermixture of Solutions of Zinc, Copper, and Cadmium Sulphates.*

162. Although not directly connected with the subject of electrical measurement of chemical affinity, it yet seemed of some interest to examine how far the volume-alterations that take place on mixing solutions of different strengths of zinc (copper or cadmium) sulphate run parallel with the thermal developments thereby caused. It might reasonably be anticipated that the much greater heat-evolution taking place on dilution of cadmium sulphate as compared with zinc or copper sulphate would be found to be concurrent with a greater amount of volume-alteration. On examining the matter, how-

\* Since these experiments were made, the third volume of Julius Thomsen's *Thermochemische Untersuchungen* has appeared; in this are given the results of this author's previously unpublished experiments on the heat of dilution of solutions of zinc and copper sulphates, and of zinc chlorides. These figures do not materially differ from those cited above; and their use, instead of those employed in this paper makes no noteworthy difference in the end conclusion that the heat of intermixture usually represents a less E.M.F. than that actually set up in any given case.

ever, this is not found to be the case ; the volume-alterations on dilution through a given range being but little different, whichever of the three sulphates be employed, in every case contraction\* taking place, even when the solution is already so far diluted as not to cause any measurable heat-evolution on mixing with water.

The observations were made with a large-bulbed dilatometer holding about 94 cubic centim. The volumes corresponding to the various graduations were determined by introducing a known weight of distilled water, and determining the level of the water in the stem—first, when the temperature was a little below 18°·5, the instrument being immersed in a large vessel of water kept agitated ; and secondly, when the temperature was a little above 18°·5. In this way the level at 18°·5 was obtained by interpolation. The weight of the contained water (reduced to a vacuum) being known, the volume in cubic centimetres occupied up to the level at 18°·5 was calculated

by the formula  $V = \frac{W}{\cdot 998602}$  ; where V is the volume in cubic centimetres, W the weight *in vacuo*, and ·998602 the weight of 1 cubic centimetre in grammes at 18°·5 (Kopp). By making a series of such observations a capacity-table was calculated for the instrument, expressing the volume in cubic centimetres at 18°·5 for each graduation. A known weight of the solution to be diluted was then introduced, and the level at 18°·5 obtained by making observations a little below and a little above that temperature, so as ultimately to obtain the volume occupied by a given weight (reduced to vacuum) of solution. Repetitions of experiments gave values according together within a range of ·00003 (3 milligrammes in 94 cubic centim.), and often within much less ; the chief source of discrepancy being in the correction for reduction to a vacuum which was altogether about 100 milligrammes, necessarily varying with the temperature and barometric pressure, so that a small error in temperature or pressure estimation made several milligrammes difference in weight-correction.

\* The rough values obtained in § 106 (Part V.) led to the conclusion that on diluting zinc- or copper-sulphate solution with water an increment in volume takes place. This is now found to be incorrect, the experimental errors of the rough observations being greater than the volume-alterations to be measured.

On the whole, the probable error of the average of some three or four repetitions of an observation was less than  $\pm 0.00001$  (1 milligramme in 94 cubic centim.).

A quantity of the solution to be diluted was then weighed up in a stoppered bottle and a weighed quantity of water added, the weighings being reduced to a vacuum: the whole was thoroughly intermixed, and the weight of a cubic centimetre of the diluted fluid determined as before in the dilatometer; the contraction was then calculated by means of the formula

$$C = \frac{W}{s_1} + \frac{w}{.998602} - \frac{W+w}{s_2};$$

where C is the contraction in cubic centimetres,

W the weight (*in vacuo*) of solution diluted,

w       "       "       " of the water added thereto,

$s_1$  the weight at  $18^{\circ}5$  of 1 cubic centim. of the solution diluted.

$s_2$  the weight at  $18^{\circ}5$  of 1 cubic centim. of the dilute fluid produced.

The following numbers will serve as an example:—

Tempera- ture.	Dilatometer reading.	Reading at 18°·5.	Cubic centim. corresponding from table of instrument.	Weight of fluid <i>in vacuo</i> .	Weight <i>in vacuo</i> of 1 cubic centim. at 18°·5*.
17·0	6·25	} 7·05	94·743	97·671	1·03090
19·7	7·70				
17·0	1·15	} 1·87	94·556	97·467	1·03088
19·3	2·25				
Mean ..... 1·03089					

\* In the course of these observations the following mean numbers were obtained, representing the weights *in vacuo* at  $18^{\circ}5$  C. of 1 cubic centim. of various solutions  $\text{MSO}_4 \cdot n\text{H}_2\text{O}$ :—

Copper sulphate.		Zinc sulphate.		Cadmium sulphate.	
$n=44.8$	1.18725	$n=19.06$	1.41699	$n=15.81$	1.59169
75.3	1.11325	19.31	1.41073	18.07	1.52829
109.9	1.078155	21.33	1.376055	18.10	1.52724
174.9	1.049195	32.3	1.25859	32.4	1.31285
276.4	1.03089	49.5	1.17310	49.4	1.21020
462.7	1.01805	98.8	1.088265	95.6	1.11082
		142.8	1.061275	162.9	1.06537
		219.1	1.03980	260.4	1.040795
		422.1	1.020215	424.4	1.02461
		466.0	1.01817		

This solution was made by mixing 53·781 grammes of copper-sulphate solution (of which one cubic centim. was similarly found to weigh 1·18725 gramme) with 232·509 grammes of water (all weights corrected to vacuum), whence

$$C = \frac{53 \cdot 781}{1 \cdot 18725} + \frac{232 \cdot 509}{\cdot 998602} - \frac{286 \cdot 290}{1 \cdot 03089} = \cdot 422.$$

The solution diluted was found by analysis\* to contain 16·525 per cent. of anhydrous  $\text{CuSO}_4$ , corresponding with  $2 \cdot 231 \text{ CuSO}_4 \cdot 100 \text{ H}_2\text{O}$ ; hence there was employed altogether  $53 \cdot 781 \times \cdot 16525 = 8 \cdot 887$  grammes of  $\text{CuSO}_4$ , or  $\cdot 0557$  gramme-molecule; so that the contraction per gramme-molecule was  $\frac{\cdot 422}{\cdot 0557} = 7 \cdot 58$  cubic centim., the diluted fluid possessing the composition  $\cdot 362 \text{ CuSO}_4 \cdot 100 \text{ H}_2\text{O}$ .

In precisely the same way the following values were obtained on diluting  $2 \cdot 231 \text{ CuSO}_4 \cdot 100 \text{ H}_2\text{O}$  to other extents:—

Solution ultimately obtained, $n \text{ CuSO}_4 \cdot 100 \text{ H}_2\text{O}$ .	Contraction in cubic centimetres per gramme-molecule.
$n = 1 \cdot 328$	2·76
$= \cdot 910$	4·40
$= \cdot 572$	6·19
$= \cdot 362$	7·58
$= \cdot 216$	8·88

Similarly the following values were obtained on diluting  $5 \cdot 247 \text{ ZnSO}_4 \cdot 100 \text{ H}_2\text{O}$  to various extents:—

$n = 4 \cdot 744$	0·96
$= 3 \cdot 096$	4·78
$= 2 \cdot 020$	7·59
$= 1 \cdot 012$	11·23
$= \cdot 700$	12·63
$= \cdot 457$	14·03
$= \cdot 237$	15·69

And the following, on similarly diluting  $6 \cdot 325 \text{ CdSO}_4 \cdot 100 \text{ H}_2\text{O}$ :—

\* The mode of analysis adopted was to evaporate to dryness a weighed quantity of solution and weigh the residual anhydrous salt after continued heating to  $300^\circ$ – $400^\circ$ , terminating in very gentle ignition for a minute or two at a red heat barely visible in the dark.

Solution ultimately obtained, $n \text{ CuSO}_4 \cdot 100 \text{ H}_2\text{O}$ .	Contraction in cubic centimetres per gramme-molecule.
$n = 5.534$	1.23
$= 3.086$	5.86
$= 2.024$	8.38
$= 1.046$	11.46
$= .614$	13.35
$= .384$	14.98
$= .235$	15.81

On graphical representation on a large scale and interpolation, the following values are deduced as the amounts of contraction taking place on diluting to the strengths  $.25 \text{ MSO}_4 \cdot 100 \text{ H}_2\text{O}$  solutions of strength  $n \text{ MSO}_4 \cdot 100 \text{ H}_2\text{O}$  :—

	Zinc sulphate.	Copper sulphate.	Cadmium sulphate.
$n = .25$	0	0	0
.5	1.8	1.85	1.75
1.0	4.25	4.5	4.0
1.5	6.35	6.4	5.95
2.0	8.0	7.95	7.4
2.25	8.65	8.55	7.95
3.0	10.8	.....	9.95
4.0	12.95	.....	11.95
5.0	15.05	.....	13.75
5.5	16.0	.....	14.5

The curves marked respectively 1, 2, and 3 (Pl. V. fig. 7) represent these values. It is evident that the contraction with cadmium solutions is always less than that with zinc- or copper-sulphate solutions, instead of greater, as might have been *a priori* anticipated from the greater heat of dilution. The difference, however, is in no case very great; whilst with zinc and copper solutions the curves almost coincide.

163. From these values the amounts of contraction on intermixture of gramme-molecules of two solutions of any one of the three salts differing in strength are readily calculable by the formula

$$C = c_1 + c_2 - 2c_3,$$

parallel with the analogous equation for heats of intermixture (§ 160); where  $C$  is the contraction on intermixture, and  $c_1$ ,  $c_2$ , and  $c_3$  respectively the contractions on dilution to the same ultimate limit of the solutions  $\text{MSO}_4 \cdot 2a \text{ H}_2\text{O}$ ,  $\text{MSO}_4 \cdot 2b \text{ H}_2\text{O}$ , and  $\text{MSO}_4 \cdot (a+b) \text{ H}_2\text{O}$ ; and more generally still the contrac-

tions are calculable that ensue when any two solutions of any pair of the three salts are intermixed. Thus, when A gramme-molecules of  $\text{MSO}_4 \cdot m\text{H}_2\text{O}$  and B gramme-molecules of  $\text{M}'\text{SO}_4 \cdot n\text{H}_2\text{O}$  are intermixed, the resulting mixture is

$$\left\{ \frac{\text{M}}{\text{M}'} \right\} \text{SO}_4 \frac{mA + nB}{A + B} \text{H}_2\text{O}.$$

If, then,  $a$  be contraction per gramme-molecule on diluting the first solution to the strength of the mixture, and  $b$  be the (negative) contraction ensuing on (negatively) diluting the second solution to the same strength, the total contraction on intermixture is  $Aa + Bb$ , and the contraction per gramme-molecule of the two salts used jointly is  $\frac{Aa + Bb}{A + B}$ . A number of experiments were made which showed that the actual contraction observed was sensibly identical (within experimental error limits) with that calculated in this way, the values of  $a$  and  $b$  being deduced from the above table by interpolation. Thus the following values were obtained:—

#### Different Solutions of the same Salt mixed.

Stronger solution.....	$\text{CuSO}_4 \cdot 47 \text{H}_2\text{O}$	$\text{ZnSO}_4 \cdot 19.3 \text{H}_2\text{O}$	$\text{CdSO}_4 \cdot 15.81 \text{H}_2\text{O}$
Weaker solution .....	$\text{CuSO}_4 \cdot 163 \text{H}_2\text{O}$	$\text{ZnSO}_4 \cdot 148 \text{H}_2\text{O}$	$\text{CdSO}_4 \cdot 171 \text{H}_2\text{O}$
Observed contraction	1.12	3.84	4.88
Calculated „	1.13	3.83	4.66
Difference .....	+ .01	— .01	— .22

#### Solutions of different Salts used.

Stronger solution.....	$\text{ZnSO}_4 \cdot 19.3 \text{H}_2\text{O}$	$\text{CuSO}_4 \cdot 47 \text{H}_2\text{O}$
Weaker solution .....	$\text{CuSO}_4 \cdot 163 \text{H}_2\text{O}$	$\text{ZnSO}_4 \cdot 148 \text{H}_2\text{O}$
Observed contraction ...	4.37	.92
Calculated „	4.23	.99
Difference .....	— .14	+ .07
$\text{CdSO}_4 \cdot 15.81 \text{H}_2\text{O}$ $\text{CuSO}_4 \cdot 163 \text{H}_2\text{O}$ 4.39 4.36	$\text{CdSO}_4 \cdot 15.81 \text{H}_2\text{O}$ $\text{ZnSO}_4 \cdot 148 \text{H}_2\text{O}$ 4.19 4.11	$\text{ZnSO}_4 \cdot 19.3 \text{H}_2\text{O}$ $\text{CdSO}_4 \cdot 171 \text{H}_2\text{O}$ 4.41 4.42
— .03	— .08	+ .01

Since but little difference exists between the contractions on dilution through given ranges, whether zinc, copper, or

cadmium sulphate be employed, it results that the amounts of contraction on intermixture when two different solutions of the same salt are mixed will not differ greatly whichever of the three salts be employed. It would hence seem that there is a much closer connexion between the amount of contraction taking place on intermixture, and the potential difference thereby developed, than there is between either of these values and the heat-evolution simultaneously taking place. For varying solution-strengths, the first two values alter fairly concurrently and to extents not widely different, whether zinc, copper, or cadmium sulphate be used. But this is by no means the case with the heat-values, the cadmium value largely exceeding the corresponding zinc and copper values, which latter two are substantially identical.

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### IX. *On an Integrating Anemometer.*

*By* WALTER BAILY, M.A.\*

[Plates VI. & VII.]

ON June 10th, 1882, I communicated to the Society a design for an integrating anemometer, and exhibited a working model†. I have now to describe the instrument itself, which I have had made by Messrs. Elliott, with the assistance of a grant from the Royal Society. The mechanical part of the instrument is seen in perspective in Plate VI. fig. 1. The base is of iron, and the rest of the instrument is chiefly of brass. On the base stand four columns C, of which only two are shown in fig. 1. These hold a table O, of which fig. 2 gives a view as seen from above. The tops of the columns C are seen in fig. 2. The table supports four columns, D, of which only two are shown in fig. 1, and of all of which the positions are shown in fig. 2. The pillars D hold the supports of a spindle A, fig. 1, which is to be connected with a vane. There is another spindle, B, which is to be connected with Robinson's cups, and which turns, by means of cogs, the large horizontal disk X, so that X will revolve with a velocity which may be taken as proportional to that of the wind. The

\* Read December 8, 1883.

† Phil. Mag. Sept. 1882; Phys. Soc. Proc. vol. v. p. 157.