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

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1879 Proc. Phys. Soc. London 3 213

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PROCEEDINGS
OF
THE PHYSICAL SOCIETY
OF LONDON.

MARCH 1880.

XXIX. *On the Determination of Chemical Affinity in terms of Electromotive Force.*—Part I. By C. R. ALDER WRIGHT, D.Sc. London, Lecturer on Chemistry and Physics in St. Mary's Hospital Medical School.

1. BETWEEN the years 1841 and 1846 Joule made a series of experiments on the development of heat during electrolysis, which led him to the conclusions:—that when a current is passed through a fluid conductor, heat is developed in accordance with the same law as that which he found to obtain with a solid metallic wire, viz. that the heat produced in a given time is proportionate to the square of the current and to the resistance of the conductor—usually known as Joule's law; that if electrolysis is produced, the actual heat developed in the electrolyte is less than that deducible from this law by a quantity precisely equal to the amount that would be given out in re-forming from its products of decomposition the compound decomposed; and consequently that it is possible to determine the "heat of formation" of a compound by the inverse method of determining the heat absorbed during its electrolysis. The actual results thus obtained, as regards the "heat of formation" of copper sulphate, zinc sulphate, and water, were communicated to the French Academy in 1846, but were not published in detail until 1852 (Phil. Mag.

[4] vol. iii. p. 481). Some few months before they appeared, Dr. Thomas Woods published (*ibid.* vol. ii. p. 268) the results of experiments showing that in the decomposition of water by electrolysis a quantity of heat is taken up approximately equal to that evolved by the recombination of the hydrogen and oxygen evolved.

2. Joule's method of operating is described by him in the following words:—"I take a glass vessel filled with the solution of an electrolyte and properly furnished with electrodes; I place the electrolytic cell in the voltaic circuit for a given length of time, and carefully observe the quantity of decomposition and the heat evolved. By the law of Ohm I then ascertain the resistance of a wire capable of obstructing the current equally with the electrolytic cell. Then by the law we have proved [*i. e.* 'Joule's law'] I determine the quantity of heat which would have been evolved had a wire of such resistance been placed in the current instead of the electrolytic cell: this theoretical quantity, being compared with the heat actually evolved in the electrolytic cell, is always found to exceed the latter considerably. The difference between the results evidently gives the quantity of heat absorbed during the electrolysis, and is therefore equivalent to the heat which is due to the reverse chemical combination by combustion or other means" (*loc. cit.* pp. 493, 494).

Put into symbols this may be thus expressed:—Let h_1 be the heat actually developed in the electrolyte by a current C_1 in a given time t during which w_1 grammes of electrolyte are decomposed. Let h_2 be the heat that would be developed in a wire of the same resistance (*i. e.* capable of equally "obstructing the current") in the same time t by the same current C_1 . Let h_3 be the heat actually developed in another wire by a different current C_2 in the same time t ; and let the resistance of the electrolytic cell be a times the resistance of this second wire. Then, by Joule's law,

$$\frac{h_2}{h_3} = \frac{C_1^2}{C_2^2} a,$$

whence the heat absorbed in decomposing w grammes of electrolyte is

$$h_2 - h_1 \text{ or } = h_3 \frac{C_1^2}{C_2^2} a - h_1,$$

and the heat absorbed in decomposing 1 gramme of electrolyte is

$$\frac{h_3 \frac{C_1^2}{C_2^2} \alpha - h_1}{w}.$$

In this way Joule obtained in three sets of observations the following mean values for the heat absorbed in the decomposition of a gramme-equivalent of water:—

	34101
	34212
	<u>32356</u>
Average . .	33557

the numbers found by direct determination of the heat of combustion of hydrogen in oxygen being close to 34100 gramme-degrees, according to the most trustworthy experiments (*vide* § 31).

3. Joule further applied this principle to the electrolysis of zinc and copper sulphates, and found that the heat actually developed in the electrolytic cell was in each case less than that which would be developed in a wire “obstructing the current” equally with the cell by a quantity sensibly equal to the heat that would be generated by the oxidation of the metal liberated during the electrolysis by the oxygen simultaneously set free, together with that produced by the solution in the dilute sulphuric acid also formed of the metallic oxide thus produced. That this should be so is an evident deduction from the principle of conservation of energy; for if the total work that could be done in the passage of a current C through a resistance R in a time t be expressed by the formula $C^2 R t$ (Joule’s law), and some of that work be performed not as heat but in undoing chemical combination, it results that the amount of work actually done as sensible heat must be just so much less than $C^2 R t$ as corresponds to the chemical work performed.

4. The experiments of Woods were of a far less accurate kind than those of Joule, but were based on much the same principles. A current being passed through an electrolytic cell for a given time, the heat developed was roughly measured and the amount of decomposition; a wire was then substituted for this electrolytic cell of such resistance that the current

passing was the same as before (the electromotor remaining the same). The heat developed in this wire being determined, was found to exceed that produced in the electrolytic cell in the same time by a quantity sensibly equal to that which would be generated by the recombination of the products of electrolysis.

The formula just deduced for Joule's method of experimenting then becomes

$$\frac{h_3 - h_1}{w},$$

for $C_1 = C_2$ and $a = 1$.

5. In 1865 Joule's results were confirmed by Raoult (*Ann. de Chim. et de Phys.* 4th series, ii. p. 317, and iv. p. 392) by a method which will be discussed later on (§ 23). The amount of heat absorbed per gramme-equivalent of water decomposed was found by Raoult to be 34028, or sensibly the same as that deduced by direct combustion; whilst similar results were obtained with copper sulphate. In 1869 Kiechl published experiments (*Wien. Akad. Ber.* lx. [2] 121) in principle the same as Joule's, but differing considerably in the details, notably in that the wire was made into a rheostat, so that its resistance could be regulated throughout the observations. As a mean of nine accordant experiments, 33653 was found to be the heat absorbed per gramme-equivalent of water decomposed. Shortly before this, Favre demonstrated in a very simple way (*Comptes Rendus*, lxvi. p. 252; *Pogg. Ann.* cxxxv. p. 300) that as much heat is absorbed during the decomposition of an electrolyte as is produced by the recombination of the products of decomposition. A small battery was enclosed in a calorimeter, and the heat produced by the solution of a given quantity of zinc determined, the current produced being made to circulate through a coil of wire also contained in the calorimeter; so that the total heat generated was determined. A voltameter was then substituted for the coil of wire, when the quantity of heat was found to be lessened by an amount equal to 34,204 gramme-degrees per gramme-equivalent of zinc dissolved, *i. e.* of water decomposed. Similarly when copper sulphate was decomposed instead of water, the heat-evolution was lessened by an amount sensibly equal to the heat evolved in the synthesis of the salt.

6. In 1851 Sir William Thomson carried the ideas suggested by the experiments of Joule and others a considerable way further. In a remarkable paper on the mechanical theory of electrolysis (Phil. Mag. 1851, vol. ii. p. 429), he demonstrated that the force of chemical affinity is expressible in terms of electromotive force, and calculated, from data largely furnished by Joule, that the work done in decomposing water corresponds to an E.M.F. of 3,305,400 foot-grain-second electromagnetic units (equal to 1.415×10^8 C.G.S. units, or 1.415 volt), that representing the sum of the chemical actions in a Daniell cell corresponding to 2,507,100 (equal to 1.074×10^8 C.G.S. units); so that the "affinity" between oxygen and hydrogen in water is $\frac{1.415}{1.074} = 1.318$ times as strong as the sum of the affinities exerted in the chemical changes going on in a Daniell cell. Similar calculations, based on more recent determinations of the values involved, lead to somewhat higher numbers, approximating to 1.502×10^8 C.G.S. units for water and 1.154×10^8 for the Daniell cell (*vide* § 16), giving the ratio $\frac{1.502}{1.154} = 1.302$.

7. The general proposition that the force of chemical affinity is expressible in terms of E.M.F. may be simply demonstrated as follows:—Let the strength of chemical combination, or the chemical work done by the force of chemical affinity, be defined as the absolute amount of work spent or gained in the synthesis from its constituents of a given weight (say 1 gramme) of the compound considered. This work may be expressed in terms of heat, and is ordinarily measured as such: thus in the synthesis of a gramme of water from gaseous oxygen and hydrogen at the ordinary pressure and temperature, an amount of work is done representing an evolution of a quantity of heat amounting, according to the most accurate determinations, to close upon 3800 gramme-degrees (§ 31); whence, taking the mechanical equivalent of heat as 42 megalergs per gramme-degree*, the work done in this synthesis is close to 16 erg-tens $= 16 \times 10^{10}$ C.G.S. units.

* The values obtained by Joule by friction of water lie somewhat below this figure (near to 41.5×10^6): whilst that deduced by him from the development of heat by electric currents in a wire of known resistance

The experiments of Faraday first demonstrated the two following laws, which have since been fully confirmed by many other experimenters:—

I. When a compound is electrolyzed, the weight of substance decomposed is proportionate to the quantity of electricity passing. [A low degree of conductivity is supposed by some experimenters to be possessed by electrolytes, of such a nature that very feeble currents can be passed through them without causing any chemical decomposition; this, however, even if admitted to be the case, would not appreciably interfere with the correctness of the foregoing proposition.]

II. When a current is passed for a given time successively through several compounds so as to electrolyze them all, it decomposes quantities of them in the ratio of simple functions of their “molecular weights,” evolving the products of decomposition, when elementary, in the ratio of simple functions of their combining numbers or “atomic weights.” The quantities of compounds decomposed and of elements evolved by a current which evolves 1 part of hydrogen from water under these circumstances are called their “equivalent values,” or, more briefly, their *equivalents*, in reference to the particular compounds decomposed.

Law I. may be thus expressed:—Let n be the number of grammes of compound decomposed, and q the quantity of electricity passing; then

$$n \propto q.$$

Law II. states that, if a be the “equivalent” of a given compound,

$$n \propto a.$$

Hence

$$n \propto aq;$$

and consequently

$$n = aq \times \chi,$$

where χ is a multiplier independent of the quantity of electricity passing, and of the value of the “equivalent” of the compound.

lies somewhat above it ($42 \cdot 10 \times 10^6$). Numbers lying somewhat above 42×10^6 have been obtained by Hirn, Violle, and Regnault (*vide* §§ 33 & 34).

When $n=a$, $\chi=\frac{1}{q}$; that is, χ is the reciprocal of the quantity of electricity requisite to decompose a gramme-equivalent of the electrolyte employed. For convenience of reference, χ may be termed the *electrochemical constant*.

8. The term "electrochemical equivalent of a substance" is employed to mean the quantity of substance decomposed by a unit quantity of electricity, *i. e.* the value of $\frac{n}{q}$ (which $=a\chi$); and the term "electrochemical equivalent of an element," in reference to such a compound, is used to indicate the quantity of that element evolved during electrolysis of that compound during the passage of a unit of electricity. If b be the equivalent of the element in reference to the compound employed, the equivalent of the compound being a , the electrochemical equivalent of the element in reference to the compound is

$$\frac{n}{q} \cdot \frac{b}{a},$$

which $=b\chi$.

n is of necessity a constant for any given compound: and so is b in many cases; that is, in such cases, no matter what compound of a particular element be electrolyzed, the same quantity of that element is set free by the passage of a unit of electricity. In other cases, however, b varies with the character of the compound employed; that is, the same quantity of element is not necessarily always evolved by the passage of a unit of electricity. For example, the value of b for hydrogen, chlorine, and silver appears to be constantly 1, 35.5, and 108 respectively; whilst for copper the value is 31.75 for compounds of the class known as cupric salts, and 63.5 for compounds of the class known as cuprous salts. When b is thus variable, its different values are always simple integral multiples of a common divisor.

9. Sir William Thomson calculated in 1851 (*loc. cit. supra*) the value of $a\chi$ for water on the foot-grain-second electromagnetic system to be as follows:—

Hence the mean of this value and that deduced by Kohlrausch from his own observations (viz. $\chi = 0.00010527$) may be taken as probably the nearest approximation to the truth; *i. e.* $\chi = 0.000105005$, or practically $\chi = 0.000105$.

10. If it were possible to obtain a current between the two electrodes of a voltameter or other similar electrolytic cell which would decompose the electrolyte without any disturbance of the thermal equilibrium, then the difference of potential between the electrodes would represent the force of chemical affinity exerted between the products of decomposition in the compound examined; for if e be the potential-difference (E.M.F. existing between the electrodes) during the passage of a quantity of electricity q , eq units of work will be done. If n grammes of substance are decomposed, and f is the work done by the force of chemical affinity in the synthesis of a gramme of substance from the products of decomposition, the total work done is also expressed by nf , which, by the definition of electrochemical equivalents (§ 8), $= a\chi qf$. Hence

$$af = \frac{e}{\chi}.$$

Or "affinity," reckoned per gramme-equivalent, is measured by electromotive force divided by a quantity which is constant; *i. e.* the work done in the synthesis of a gramme-equivalent of substance is expressible by a value indicated in electromotive-force units, just as it is expressible by a value indicated in heat units—the one valuation involving the constant χ , the other J .

11. In practice it is impossible to realize this supposition; for experiment shows that, in the passage of electricity between two electrodes, work is done not only as chemical decomposition but also as heat; by determining the amount of the latter, however, it is easy to calculate how much of the total potential-difference existent between the electrodes is due to the chemical affinity of the constituents: thus, if h gramme-degrees are evolved during the decomposition of n grammes of substance of electrochemical equivalent $a\chi$ by the transfer of a quantity of electricity q , and if E represent the total potential-difference existent between the electrodes, the total work done in the electrolytic cell is Eq , of which hJ is done as heat. Hence

$Eq - hJ$ is done as chemical decomposition. Let this be equal to eq , where e is the E.M.F. representing the chemical affinity to be measured ; then

$$e = E - \frac{hJ}{q} = E - hJ \frac{a\chi}{n},$$

since, by definition of electrochemical equivalents (§ 8),

$$q = \frac{n}{a\chi}.$$

Finally, therefore,

$$e = E - H\chi J,$$

where

$$H = \frac{ha}{n},$$

i. e. where H is the heat evolved per gramme-equivalent of substance decomposed.

Experiments made in this way (detailed in Part II., *vide* also § 32) have given numbers for the value of e in the case of water closely corresponding with the value of e deducible from direct combustion-experiments by the formula arrived at above (§ 10), viz.

$$af = \frac{e}{\chi},$$

which becomes

$$e = af\chi = ah'J\chi = H'\chi J,$$

where h' is the heat liberated per gramme, and H' that per gramme-equivalent of water formed by combustion of hydrogen and oxygen.

12. On attentively considering the phenomena attendant on electrolysis, it is evident that it by no means follows that the direct action of the current causes the entire change taking place ; physical changes of state and chemical actions secondary to those due to the action of this current alone may occur ; so that the value of e thus deduced, although representing the E.M.F. corresponding to the *nett work done* in the sum of the total changes taking place, and consequently representing the "affinity" between the ultimate products in the original compound as above defined, *is not necessarily a measure of the tendency to combine together of the substances primarily formed by the electrolytic decomposition.* For instance, suppose that in

the electrolysis of water the primary products are ordinary gaseous hydrogen and ozone, the latter becoming subsequently transformed (by a secondary chemical action) into ordinary gaseous oxygen: then, since heat is evolved in the conversion of ozone into oxygen to the extent of 14,800 gramme-degrees per 24 grammes of oxygen (Berthelot, *Bull. Soc. Chim. Paris*, 1876, vol. xxvi. p. 56), or 4933 gramme-degrees per 8 grammes of oxygen (corresponding to 9 grammes of water), the value of e deduced as just indicated will be below the true value by an amount equal to $\frac{4933}{34100} = 14.5$ per cent.; for the negative term in the expression $E - H\chi J$ will have been overestimated by that quantity.

Again, suppose that the water is brought by a secondary physical action into a quasi-vaporous state before it is decomposed by the current into gaseous hydrogen and oxygen (*e. g.* on the molecular theory of the constitution of matter, suppose that only detached molecules of water are operated on by the current, and not the water *en masse* in the liquid state); since about 600 gramme-degrees are required to volatilize a gramme of water at the ordinary temperature (the latent heat of steam at near 15° being about 600), or 5400 per gramme-equivalent, the value of e deduced as above will be too large by about $\frac{5400}{34100} = 15.8$ per cent, because in this case the negative term $-H\chi J$ will be underestimated to that extent.

Consequently, if both secondary actions be supposed to take place (*i. e.* if the electrolysis proper takes place between detached molecules of water converting them into gaseous hydrogen and ozone), the value of e will be $15.8 - 14.5$, or 1.3 per cent. too large.

Suppose, again, that the primary electrolytic action is to convert liquid water into *liquid* oxygen and hydrogen, and that the conversion of these liquefied elements into the ordinary gaseous condition is due to secondary physical changes; it is evident that the value of e found as above is too large by $\frac{h_1}{34100} \times 100$ per cent., where h_1 represents the heat that is absorbed in the vaporization of a gramme-equivalent of each of the liquefied gases taken together.

Yet again, in the electrolysis of copper sulphate, suppose

that whilst the ultimate chemical change is expressed by the equation

this change is actually the sum of two changes, of which the first is secondary:—

it is evident that the value of e deduced as above will be greater than that corresponding to the second change only, by an amount equivalent to the heat absorbed during the first change.

13. During the last three or four years the writer has made various experiments with the view of determining the E.M.F. measuring the "affinity" between various constituents in different compounds (especially oxygen and hydrogen in water), not only when the substances developed by the electrolysis are in their ordinary conditions, but also when they are "nascent"—i. e. with the view of determining, first, the E.M.F. corresponding to the "heat of formation" of (for instance) water from gaseous oxygen and hydrogen, and, secondly, that requisite to produce electrolysis proper *apart from secondary physical and chemical changes*. It is evident that, if such determinations are practicable, the comparison of the two sets of values might lead to interesting conclusions as to the nature of these secondary actions, and might throw light on the internal mechanism of the chemical changes taking place, and especially on the phenomena connected with the "nascent state." Results in this direction have already been obtained by Favre, with this difference, that the values are expressed in gramme-degrees, being obtained entirely by calorimetric observations. The discussion of the observations of this kind already made by previous experimenters, and of the writer's results (obtained chiefly by electrical measurements), will be resumed in a future paper, the present essay having chiefly reference to the determination of the E.M.F. representing the sum of the physical and chemical actions taking place during electrolysis. It should, however, be noticed in connexion with this subject, that since Sir William Thomson first sketched out the Mechanical Theory of Electrolysis (*loc. cit. supra*), more exact measurements have shown that the E.M.F. actually capable of being generated by a given voltaic combination is by no

means necessarily equal to the sum of the physical and chemical changes taking place in the pile, and that it is not necessarily constant for the same ultimate chemical change—varying with the temperature, the state of dilution of the solutions used, &c.

14. For example, when zinc is dissolved in dilute sulphuric acid, the total ultimate change is expressed by the equation

which corresponds to an evolution of somewhat more than 18,000 gramme-degrees per gramme-equivalent of zinc dissolved or of hydrogen liberated, and representing therefore about $18000 \times 0.000105 \times 42 \times 10^6 = 0.794 \times 10^8$ C.G.S. units of E.M.F., or about 0.794 volt. Similarly, when zinc or any analogous metal is dissolved in any other acid (*e. g.* hydrochloric) with evolution of hydrogen by a parallel reaction, a heat-evolution of h gramme-degrees results per gramme-equivalent, corresponding to $h\chi J$ C.G.S. units of E.M.F. But when this change takes place in an electromotor with a second metal as the other plate, the E.M.F. actually set up by the tendency to produce this ultimate change varies with the nature of the second metal; and whilst the E.M.F. produced is rarely, if ever, precisely equal to $h\chi J$ even at first, when a current has been made to circulate for some short time the E.M.F. is found to have diminished to an amount depending on the rate of evolution of hydrogen on the surface of the other plate, the character of its surface, the temperature, &c. This is usually expressed by saying that the plates become “polarized,” or that a “counter electromotive force” x is set up, diminishing the effective E.M.F. of the arrangement from E , which it was at first, to $E - x$, the value of x varying with circumstances.

From the principle of the conservation of energy it results that, when the current circulates, the difference between the work $h\chi J \times Q$ which would be performed during the passage of a quantity of electricity Q sufficient to decompose a gramme-equivalent of substance, and $(E - x)Q$ the work which the current can actually perform, must make its appearance as sensible heat. If, therefore, $E - x < h\chi J$, the electromotor must rise in temperature from this cause—irrespective of the rise due to the fact that, as the current traverses the electromotive

equally with the rest of the circuit, heat is developed therein in proportion to its resistance in accordance with Joule's law (§ 1). If, however, $E - x > h\chi J$, the battery is of necessity proportionately cooled; and if the experiment is so carried out that the resistance of the battery is small compared with that of the rest of the circuit, so that the heat developed in the battery in accordance with Joule's law is but small, the cooling effect may be made to preponderate over the heating effect, so that an absorption of heat on the whole takes place in the battery.

15. This effect has been experimentally studied by Favre (*Comptes Rendus*, lxvi. p. 252, lxvii. p. 1012, lxviii. p. 1300, and lxix. p. 34), who has shown that under the last-named conditions an absorption of heat takes place during the solution of zinc or cadmium in hydrochloric acid, whilst heat-evolution takes place if sulphuric acid be substituted for hydrochloric. In other words, the secondary actions set up, as a whole, absorb heat in the first case and evolve it in the second. Similarly in two-fluid batteries, such as Daniell's and Grove's, analogous results were obtained, although in these cases "polarization" by evolution of hydrogen could not possibly be produced. With cells after Daniell's construction heat was found to be evolved by the secondary actions, though not to a very large extent (about 4·3 per cent. of the heat due to the consumption of zinc and precipitation of copper); whilst with a Grove's battery a considerably larger heat-absorption took place, amounting to about 11·9 per cent., of the heat due to solution of zinc and reduction of nitric acid.

16. This result with a Daniell cell is borne out by experiments of a different kind. The E.M.F. which a Daniell cell is practically capable of giving has been variously estimated by different observers, at from 1·05 to 1·14 volt, 1·10 to 1·12 being a usual average. The E.M.F. corresponding to the heat evolved in the reaction

(which expresses the ultimate change in a Daniell cell, apart from local action) is several per cent. higher. Thus Favre estimated the heat thus evolved per gramme-equivalent to be 27,388 (*Comptes Rendus*, lxiii. p. 369), and subsequently as 25,060 (*ibid.* lxix. p. 35): the mean of these two numbers is

26,224, corresponding to an E.M.F. of $26,224 \times 0.000105 \times 42 \times 10^6 = 1.156 \times 10^8$ C.G.S. units, or 1.156 volt. Julius Thomsen has calculated (*Berichte deut. chem. Ges.* 1872, vol. v. p. 170) from his own determinations, together with those of Andrews, Dulong, Hess, and Favre and Silbermann, that the heat-evolutions taking place during the formation of zinc sulphate and copper sulphate are respectively 108,460 and 56,216 per "gramme-molecule" (these formations being expressed in Thomsen's symbols thus—Zn, O, SO₃, aq, and Cu, O, SO₃, aq). Hence the heats are 54,230 and 28,108 per gramme-equivalent; whence the displacement of copper from copper sulphate by metallic zinc, forming copper and zinc sulphate, must give rise to an evolution of $54,230 - 28,108 = 26,122$ gramme-degrees per gramme-equivalent, corresponding to $26,122 \times \chi J = 1.152$ volt.

17. Results analogous to those of Favre have also been obtained by Raoult (*Ann. de Chim. et de Phys.* 4th series, ii. p. 317, and iv. p. 392)—some forms of voltaic combinations giving rise to the production of more heat outside the battery than corresponds to the heat evolved by the ultimate chemical and physical changes taking place therein, and others to less. Raoult found that the current from the Daniell cell used by him was capable of doing total work equal to 23,900 gramme-degrees per gramme-equivalent of zinc dissolved in each cell: this represents only $23,900 \times \chi J = 1.054$ volt, a quantity less by 8.5 per cent. than the value calculated above from Thomsen's figures as the E.M.F. corresponding to the sum of the chemical and physical actions taking place in the cell.

To express the difference between the heat actually producible by the sum of the chemical and physical actions taking place in an electromotor and that corresponding to the current actually obtainable from the electromotor, Raoult calls the first the *chemical heat* of the pile, and the latter the *voltaic heat* thereof; whilst the terms *chemical heat* and *galvanic heat* have been employed by Edlund to indicate these quantities respectively (*Phil. Mag.* 1877, vol. iii. pp. 428 & 501); so that the above results may be indicated by saying that the chemical heat of a Daniell battery is 26,122 gramme-degrees (per gramme-equivalent of zinc dissolved), whilst the voltaic or galvanic heat is 23,900, and so on. Several points touched

upon in these papers are of interest as bearing on the problem of the determination of the amount of E.M.F. corresponding to the primary effects of electrolysis; their discussion, like that of several analogous memoirs by previous observers, is postponed till a later occasion.

18. In order to apply the general method above indicated (§ 11) for the determination of the E.M.F. corresponding to the sum of the chemical and physical actions taking place during electrolysis, it is requisite to determine:—first, the difference of potential subsisting between the electrodes; secondly, the quantity of electricity passing in a given time (known from the weight of substance decomposed); and, thirdly, the heat evolved as such in the electrolytic cell in that time. The first quantity may be found approximately by the aid of a sine galvanometer of very high resistance. A method which is in principle substantially this has already been used by Raoult (*loc. cit.*); this will be more fully discussed further on (§ 23).

Another way of determining it may be based upon observations with a voltmeter, thus:—The amount of decomposition produced in a given time t by passing a current from the battery employed (of E.M.F. = E') through the voltmeter is noticed = n_1 ; the electrolytic cell is then placed also in circuit, and the amount of decomposition in the voltmeter in the same time t again determined = n_2 , and also the heat produced in the cell = h . R being the resistance of the battery, voltmeter, and connexions, and r being the resistance of a wire “obstructing the current equally with the electrolytic cell,” the currents flowing in the two cases are respectively

$$C_1 = n_1 \times k = \frac{E'}{R} \quad \text{and} \quad C_2 = n_2 \times k = \frac{E'}{R + r},$$

where k is a constant—whence

$$\frac{R}{R + r} = \frac{n_2}{n_1}, \quad \text{and} \quad \frac{r}{R + r} = \frac{n_1 - n_2}{n_1}.$$

The difference of potential set up between two points connected by a medium of resistance r traversed by a current C_2 is

$$rC_2 = \frac{r}{R + r} E' = \frac{n_1 - n_2}{n_1} E';$$

and hence the expression for the E.M.F. equivalent to the affinity to be found, $E - H\chi J$, becomes

$$\frac{n_1 - n_2}{n_1} E' - \frac{ha\chi J}{n_2},$$

where a is the equivalent of water = 8.98.

19. Experiments on the electrolysis of water have been made by the writer in accordance with this method, and have furnished moderately concordant results approximating to the value of the E.M.F. representing the affinity to be measured, calculated from the heat of combustion of hydrogen (§ 32); but as the experimental errors attendant on the method are considerably greater than those involved when the value of $\frac{r}{R+r} E'$ is directly determined by means of a quadrant electrometer, this latter mode of operating has been adopted in preference: the details of observations thus made in the case of water are given in Part II. Meanwhile it is of interest to notice that if a tangent galvanometer be substituted for a voltmeter (the quantity of electricity passing being determined by observing the quantity of electrolyte w decomposed whilst a quantity of heat h is evolved), the value of the affinity to be determined is given by the analogous formula

$$e = \frac{\tan \alpha - \tan \beta}{\tan \alpha} E' - \frac{ha\chi J}{w},$$

where α and β are the deflections observed with the currents C_1 and C_2 respectively. The experiments of Joule above referred to (Phil. Mag. vol. iii. p. 481), although made for the purpose of calculating the heat of formation of water, copper sulphate, and zinc sulphate in a wholly different way, contain the data requisite for the application of this mode of observation, based on the use of the tangent galvanometer; it being taken for granted that E' , the value of the E.M.F. of the Daniell battery used, was $m \times 1.10$ volt, where m is the number of cells used in the experiment recalculated. Thus, Joule found the following numbers in a series of four observations on the electrolysis of water in which six Daniell cells were used:—

	Mean $\tan \alpha$.	Mean $\tan \beta$.	Gramme of H evolved.	Rise of thermometer.
	3.4170	1.6234	0.03978	40.6 scale divisions.
	3.9429	1.7780	0.04212	37.8 " "
	4.3412	1.8374	0.04372	41.7 " "
	4.0508	1.8011	0.04411	38.8 " "
Average	3.9380	1.7600	0.04243	39.725
		Correction for radiation...	+ 0.656	
				<u>40.381</u>

The water-equivalent of the calorimeter was found to be 1155 grammes, whilst 23.38 scale-divisions of the thermometer represented 1° ; hence

$$h = 1994.9.$$

The E.M.F. of affinity to be found, then, is

$$\frac{3.9380 - 1.7600}{3.9380} \times 6 \times 1.10 \times 10^8$$

$$= \frac{1994.9 \times 1 \times 0.000105 \times 42 \times 10^6}{0.04243},$$

or

$$1.577 \times 10^8 \text{ C.G.S. units} = 1.577 \text{ volt.}$$

The value deduced from Joule's own figures by his mode of experimenting is 34,101 gramme-degrees per gramme-equivalent of water decomposed, representing $34101 \times \chi J = 1.504$ volt; whilst the value deducible from the best determinations of the heat evolved in the combustion of hydrogen is 34,100, representing 1.504 volt (§ 32). In two other similar sets of observations, Joule obtained the values 34,212 gramme-degrees corresponding to 1.509 volt, and 32,356 gramme-degrees corresponding to 1.427 volt. Unfortunately the data for recalculating these values, as has just been done with the first set, are not given in his paper; still the difference between the values of the E.M.F. of affinity, calculated as above and from Joule's heat-values, is apparently no greater than the differences observed in these latter on repetition. It is noticeable that a small error in the value of the E.M.F. of the battery produces a much larger error in that of the calculated result: thus, if in the set of observations recalculated as above the E.M.F. of a Daniell cell be taken as 1.08 instead of 1.10 volt, the calculated E.M.F. of affinity comes out 1.511 instead of 1.577 volt; *i. e.* a diminution of less than 2 per

cent. in the value of the Daniell cell makes a diminution of more than 4 per cent. in the E.M.F. of affinity.

20. In just the same way Joule's experiments on copper sulphate and zinc sulphate may be applied by means of the above formula. Thus with copper sulphate the following numbers were obtained, a battery of 4 Daniell cells being used :—

	Mean tan α .	Mean tan β .	Gramme of copper deposited.	Rise of thermometer.
	3.4006	0.7275	0.5686	20.4
	3.7510	0.7535	0.5777	19.4
	3.8538	0.7650	0.5881	19.45
	3.8084	0.7968	0.6153	17.4
Average	3.7035	0.7607	0.5874	19.162
			Correction for radiation ...	-0.049
				19.113

In these experiments the water-equivalent of the calorimeter was 1179.2, whence $h=963.99$, and the E.M.F. representing the total chemical and physical changes is

$$\frac{3.7035 - 0.7607}{3.7035} \times 4 \times 1.10 \times 10^8 - \frac{963.99 \times 31.75 \times \chi J}{0.5874},$$

or $1.198 \times 10^8 + 10^8$ C.G.S. units or 1.198 volt.

With zinc sulphate the following numbers were obtained, a battery of 7 Daniell cells being used :—

	Mean tan α .	Mean tan β .	Gramme of zinc deposited.	Rise of thermometer.
	3.5500	0.7167	0.5797	32.2
	4.0133	0.7092	0.5647	30.0
	3.8356	0.7573	0.6010	31.3
	3.9025	0.7548	0.5991	30.5
Average	3.8254	0.7345	0.5861	31.0
			Correction for radiation ...	-0.016
				30.984

In these experiments the water-equivalent of the calorimeter was 1180.9, whence $h=1565$, and the E.M.F. to be found is

$$\frac{3.8254 - 0.7345}{3.8254} \times 7 \times 1.10 \times 10^8 - \frac{1565 \times 32.5 \times \chi J}{0.5861},$$

or

 2.395×10^8 C.G.S. units, = 2.395 volts.

21. These numbers 1.198 and 2.395 volts lie close to those calculated from Joule's figures by his own method of experimenting, and also to those calculated from the heat evolved in the synthesis of copper and zinc sulphates from the metal, oxygen, and dilute sulphuric acid; these latter quantities were found by Thomsen (*Deut. chem. Ges. Berichte*, 1872, vol. v. p. 170) to be respectively 56,216 and 108,460 per "gramme-molecule," or 28,108 and 54,230 per gramme-equivalent. A somewhat smaller number than the former of these (viz. 26,568) was found by Favre for the "heat of formation" of copper sulphate from copper, oxygen, and dilute sulphuric acid by the method referred to in § 5. These various results may be thus contrasted:—

Copper Sulphate.				
Observers furnishing the principal data for calculation.	Nature of method of calculation.	Heat evolved.		E.M.F. of affinity in volts (1 volt = 10^8 C.G.S. units).
		Per gramme of metal deposited.	Per grm.-equivalent of metal deposited.	
Joule	Joule's own method, described in §§ 2 & 3.	836.4	26556	1.171
"		856	27178	1.199
"		796.5	25289	1.115
		829.6	26341	1.162
Joule	From formula $e = E - H\chi J$ (§ 11).			1.198
Julius Thomsen			28108	1.240
Favre			26568	1.172
	From formula $e = H'\chi J$ (§§ 10 & 11).			
	"			
Zinc Sulphate.				
Joule	Joule's own method (§§ 2 & 3).	1523.1	49501	2.183
"		1547	50277	2.217
"		1619	52617	2.320
		1563.0	50798	2.240
Joule	From formula $e = E - H\chi J$ (§ 11).			2.395
Julius Thomsen			54230	2.392
	From formula $e = H'\chi J$ (§§ 10 & 11).			

22. In reference to Julius Thomsen's values, it is noticeable that some slight uncertainty in the precise values of the heat-developments in the syntheses $\text{Cu, O, SO}_3\text{aq.}$ and $\text{Zn, O, SO}_3\text{aq.}$ is introduced by the circumstance that these values are calculated from determinations of the heat evolved by the direct combustion of metal to oxide, and that produced by solution of the metallic oxide in dilute sulphuric acid—these determinations being made by different observers necessarily working with different specimens of metallic oxides, and their results being averaged. Ditte has shown, however (*Comptes Rendus*, lxxii. pp. 762 & 878, and lxxiii. p. 108), that the heat developed by dissolving a metallic oxide in an acid varies with the degree of heat to which the oxide has previously been exposed. Thus, with zinc oxide and dilute sulphuric acid, the following values were obtained per gramme-equivalent:—

	Gramme-degrees.
Zinc oxide previously heated to 350°	9,890
" " " dark red heat .	11,016
" " " bright " .	12,138

The value of this "heat of solution" was given by Favre as 10,455, and by Julius Thomsen as 11,705, the temperature to which the zinc oxide had been previously heated not being stated.

23. The experiments of Raoult above adverted to (§ 18) were conducted as follows:—A current from a Daniell battery was passed through a galvanometer and a voltameter placed in a calorimeter, a derived circuit containing a sine galvanometer being also applied to the voltameter-plates; so that the current in this derived circuit virtually measured the difference of potential subsisting between the voltameter-plates. Calling f the "intensity of the derived current," and d that due to a Daniell cell working through the same resistance, and taking 23,900 as the "galvanic heat" (§ 17) of each Daniell cell used, the total work done in the voltameter per gramme-equivalent will be represented by $\frac{f}{d} \times 23,900$ gramme-degrees: subtracting this from the heat actually developed as such, a value in gramme-degrees is obtained representing the work done as chemical decomposition. In this way Raoult ob-

tained the following values for the chemical decomposition of water and copper sulphate:—

Water.			Copper sulphate.		
33,858 gramme-degrees.			30,407 gramme-degrees.		
34,229	„	„	29,765	„	„
33,998	„	„	29,683	„	„
Mean . 34,028	„	„	29,951	„	„

These mean values correspond respectively to 34,028 $\chi J = 1.501$ volt and 29,951 $\chi J = 1.321$ volt. The former number closely agrees with the above-cited results of Joule, Kiechl, and Favre, and with the number deduced by direct combustion of hydrogen (§ 32); the latter is somewhat larger than the values deducible from the observations of Joule, Julius Thomsen, and Favre, given in § 21.

The mode of calculation employed by Raoult, however, was far less simple than would appear from this brief account of his results. He complicated the work by attempts to measure the amount of polarization set up in the voltameter; and from the numbers thus obtained, together with the strengths of the derived currents and the amounts of heat actually generated as such, he calculated certain amounts of heat, to which he applied the terms “local heat” and “voltaic heat of the voltameter,” the difference between which represented the heat equivalent to the chemical decomposition—*i. e.* the above numbers. On revising his formulæ, however, it becomes evident that the determination of the amount of polarization of the voltameter-plates (a determination the accuracy of which is open to some criticism) is in no way involved in the determination of the heat equivalent to the chemical decomposition, inasmuch as the terms involving the amount of polarization in the expressions for the “local heat” and the “voltaic heat of the voltameter” are identical, and consequently become both eliminated in the expressions representing the difference between these two quantities—*i. e.* the chemical decomposition.

24. It is evident that any method that will give a direct valuation by electrical measurements of the work done in the formation of a given compound in terms of E.M.F. will, when compared with the direct determination of the “heat of

formation" of the same compound by means of the calorimeter, enable a new valuation to be deduced for J , the mechanical equivalent of heat; for the work done in the formation of a gramme-equivalent of the compound being found by the one method to be measured by e C.G.S. units, and by the other by h gramme-degrees, the relationship

$$hJ = eQ = \frac{e}{\chi}$$

holds, where Q is the quantity of electricity requisite to decompose a gramme-equivalent of substance, *i. e.* where $Q = \frac{1}{\chi}$ (§ 7); whence

$$J = \frac{e}{h\chi}.$$

If, however, the value of J is included in the value of e , as is necessarily the case when e is calculated by the formula $e = E - H\chi J$ (§ 11), this formula becomes

$$hJ = \frac{E - H\chi J}{\chi},$$

whence

$$J = \frac{E}{(H + h)\chi}.$$

25. In the case of water, a number of determinations of h (the heat evolved by the union of oxygen and hydrogen by combustion) have been made by various observers, but for the most part with slightly different values for the heat unit. Leaving out of sight the first approximate determinations of Dulong, Hess, and Grassi (respectively 34,743, 34,792, and 34,666 gramme-degrees per 9 grammes of water formed), the following comparisons of these different determinations may be made, reducing them all, as far as possible, to the same conditions—*viz.* supposing the oxygen and hydrogen originally used per gramme-equivalent of water (respectively 7.98 and 1 gramme) and the water produced (8.98 grammes) to be all at 0° and 760 millims., the value of a gramme-degree being defined as the heat required to raise 1 gramme of water from 0° to 1° C.

The most recent of these determinations is that of Schuller and Wartha. By introducing hydrogen and oxygen at 0° into

a slightly modified Bunsen's ice-calorimeter, burning them, and weighing accurately the water formed, these observers found (Pogg. *Ann.* [2] ii. p. 359), as the mean of four closely concordant valuations, that when 8.98 grammes of water are produced from 1 gramme of hydrogen and 7.98 of oxygen, the materials and products formed being all at 0° and 760 mil-lims., the heat produced is sufficient to raise 341.261 grammes of water from 0° to 100° ; *i. e.* defining what they term a "mean calory" to be $\frac{1}{100}$ of the heat required to raise a gramme of water from 0° to 100° , the heat developed is 34126.1 "mean calories." According to Regnault (*Mémoires Acad. Sciences*, 1847, vol. xxi.), the specific heat of water at various temperatures is given by the formulæ

$$Q = t + 0.00002t^2 + 0.0000003t^3,$$

$$S = 1 + 0.00004t + 0.0000009t^2;$$

where Q is the quantity of heat required to raise a unit of weight of water from 0 to t , and S is the specific heat at t° ; so that the mean specific heat between 0° and 100° (*i. e.* the value of a "mean calory") is 1.005. On the other hand, Bosscha has revised the data on which Regnault founded his formulæ (Pogg. *Ann.* Jubelbd. p. 549), and gives the two following expressions for the quantities Q and S :—

$$Q = t + 0.00011t^2,$$

$$S = 1 + 0.00022t;$$

whence the mean specific heat between 0° and 100° is 1.011, a value largely exceeding Regnault's. Employing Regnault's value, the heat-evolution observed by Schuller and Wartha becomes $34126.1 \times 1.005 = 34,297$ gramme-degrees; whilst if Bosscha's formula be employed (as was done by Schuller and Wartha in comparing their results with those of other observers) the heat evolution becomes $34126.1 \times 1.011 = 34,501$ gramme-degrees.

26. Shortly before these experiments were published, von Than found, by nearly the same mode of operating, that 1 gramme of hydrogen and 7.98 of oxygen, at 0° and 760 millims., liberate, in forming water, 33,928 gramme-degrees (*Deut. chem. Ges. Ber.* 1877, vol. x. p. 947). The chief difference between his experiments and those of Schuller and Wartha was that, whilst the latter weighed the mercury

sucked into the calorimeter through the melting of the ice, von Than measured it in a capillary tube according to Bunsen's plan, using Bunsen's value for a gramme-degree as above defined in terms of mercury sucked in. Schuller and Wartha calculate, from Bunsen's data, that the quantity of mercury corresponding to a "mean calory" is 0.01541 gramme, whilst their own determinations give 0.015442; von Than used values corresponding to the former number, whilst Schuller and Wartha employed the latter. The differences between each of the values used and the true value are included in the experimental errors of determination in the two heat-evolutions—viz. 34,297 (Regnault) or 34,501 (Bosscha), found by Schuller and Wartha, and 33,928 observed by von Than.

27. A few years previously Julius Thomsen found (*Pogg. Ann.* 1873, vol. cxlviii. p. 368), from three accordant observations, that the formation of 17.96 grammes of water from dry oxygen and hydrogen, all materials and products being at near to 18° , produces an evolution of heat sufficient to raise the temperature of 68,207 grammes of water 1° , the water being to start with at close to 18° ; the heat required to raise the temperature of the water produced being allowed for in the determination. From Regnault's formula (§ 25) the specific heat of water at 18° is 1.00101, and from Bosscha's 1.00396; so that this observed heat-evolution corresponds to $34103.5 \times 1.00101 = 34138$, or to $34103.5 \times 1.00396 = 34239$ gramme-degrees per 8.98 grammes of water, according as the specific heat of water is calculated from the one or the other formula. If, however, the combination of the oxygen and hydrogen took place at 0° (producing water at 0°) instead of at 18° throughout, the amount of heat-evolution would be increased by $a-b$; where a is the heat given out by 8.98 grammes of water in cooling from 18° to 0° , and b the amount of heat required to raise 1 gramme of hydrogen together with 7.98 grammes of oxygen from 0° to 18° . Since the specific heats for equal weights under constant pressure of oxygen and hydrogen are respectively 0.218 and 3.405, the value of $a-b$ is sensibly 69 gramme-degrees; so that Thomsen's value becomes 34,207 if Regnault's formula is used, and 34,308 if Bosscha's be employed.

28. Favre and Silbermann found (*Annales de Chimie* [3], xxxiv. p. 357) that when 9 grammes of water were formed from oxygen and hydrogen, the gases being at a mean temperature of 9° (at 6° to commence with and 12° to end with), and the water produced being at 6° (the heat required to raise the temperature of the water produced being taken into account in determining the water-equivalent of the calorimeter), the average heat-evolution sufficed to raise 34,462 grammes of water 1° , the water being at the average temperature of 9° . According to Regnault's formula the specific heat of water at 9° is 1.00043, and according to Bosscha's 1.00198; whence the heat-evolution per 8.98 grammes becomes

$$\frac{8.98}{9} \times 34462 \times 1.00043 = 34400,$$

or

$$\frac{8.98}{9} \times 33462 \times 1.00198 = 34453,$$

according as the one or the other formula is used. To this must be added a quantity $c-d$ to reduce the value to that which would have been produced had the gases and water produced been all at 0° : c is the heat given out by 8.98 grammes of water in cooling from 6° to 0° , whilst d is the heat required to raise the hydrogen and oxygen from 0° to 9° ; whence $c-d$ is sensibly 8 gramme-degrees. So that the heat-evolution becomes 34,408 by Regnault's formula, and 34,461 by Bosscha's formula.

29. Andrews found (*Phil. Mag.* 1848, vol. xxxii. p. 321) that a litre of dry hydrogen gas at 0° and 760 millims., in combining with oxygen, the gases being at the average temperature of $19^{\circ}.7$, produced (on an average of four accordant experiments) enough heat to raise 3036 grammes of water 1° , the water being at an average temperature of $20^{\circ}.7$, and the calculation not including the heat required to raise the water produced from the average initial temperature of $19^{\circ}.7$ to the average final temperature $21^{\circ}.8$. Since a litre of hydrogen at 0° and 760 millims. weighs 0.089578 gramme (Regnault), the corrected heat-evolution per gramme of hydrogen burnt (*i. e.* per 8.98 grammes of water produced) would suffice to heat $\frac{3036}{0.089578} + 19 = 33,911$ grammes of water 1° , the water

being at $20^{\circ}7$. According to Regnault's formula the specific heat of water at $20^{\circ}7$ is $1\cdot00122$; according to Bosscha's formula, $1\cdot00455$. Hence the heat-evolution is $33911 \times 1\cdot00122 = 33952$ (Regnault's formula), or $33911 \times 1\cdot00455 = 34065$ (Bosscha's formula). To this must be added a quantity $e-f$ to reduce the value to that which would have been produced had the gases and water formed been all at 0° , e being the heat given out by $8\cdot98$ grammes of water in cooling from $19^{\circ}7$ to 0° , and f that required to heat up the constituent hydrogen and oxygen from 0° to $19^{\circ}7$; so that $e-f$ is sensibly 76 gramme-degrees; whence finally the heat-evolution becomes $34,028$ by Regnault's formula, and $34,141$ by Bosscha's formula.

30. These reduced values may therefore be thus contrasted:—

	By Regnault's formula.	By Bosscha's formula.
Schuller and Wartha	34297	34501
Von Than	33928	33928
Julius Thomsen	34207	34308
Favre and Silbermann	34408	34461
Andrews	34028	34141
Mean	<u>34174</u>	<u>34268</u>

That is, the average of these different determinations indicates that by the combustion of 1 gramme of hydrogen and $7\cdot98$ grammes of oxygen to water, the gases and water produced being at 0° and 760 millims. throughout, the heat produced would raise the temperature of $34,174$ or $34,268$ grammes of water from 0° to 1° C., according as Regnault's or Bosscha's formula for the specific heat of water is used. It is noticeable that the latter formula makes Schuller and Wartha's most carefully made experiments appear abnormal, by showing a much greater divergence, both from von Than's (made by essentially the same method) and from the general average, than is the case when Regnault's formula is employed; and hence an additional reason is derived for viewing Bosscha's alleged corrections of Regnault's numbers as being more open to objection than these numbers themselves.

If the combination of the oxygen and hydrogen be supposed to take place at 20° instead of 0° (*i. e.* if the gases used and water produced be all at 20°), the heat-evolution will be less

than that calculated above by $g-h$ gramme-degrees, where g is the heat required to raise 8.98 grammes of water from 0° to 20° , and h that requisite to raise the constituent gases through the same range, *i. e.* where $g-h$ = sensibly 77 gramme-degrees. Whence, if water be decomposed at 20° and 760 millims. into oxygen and hydrogen at the same temperature and pressure, the heat-absorption is 34,097, using Regnault's formula, and 34,191 using Bosscha's formula. Similarly at 15° , the correction $g-h$ would be 58 gramme-degrees, giving the values 34,116 (Regnault's formula), and 34,210 (Bosscha's formula).

31. On the other hand, experiments have been cited above (§§ 2 & 5), made by Joule, Kiechl, Raoult, and Favre, giving the following values for the heat-absorption during the electrolysis of water at the ordinary temperature:—

Joule	33557
Kiechl	33653
Raoult	34028
Favre	34204
Mean	33860

As these values are mostly calculated per 9 grammes of water, this average value should be reduced in about the proportion of $\frac{8.98}{9}$; but since the increase of temperature of the calorimeter observed represents a slightly higher number of gramme-degrees than that stated, on account of the increase of the specific heat of water with the temperature, the average value requires slightly raising from this cause. After making all probable allowances for these corrections, however, the mean value still remains perceptibly lower than that calculated as above from the results of Schuller and Wartha, von Than, Julius Thomsen, Andrews, Favre, and Silbermann.

On the whole, the data at present extant may be taken to show that *when 8.98 grammes of water are formed from gaseous oxygen and hydrogen at the ordinary temperature (15° to 20°) throughout, the evolution of heat is sensibly that required to raise the temperature of 34,100 grammes of water from 0° to 1° C; or when 1 gramme is formed, the heat-evolution suffices to raise 3797 (or practically 3800) grammes from 0° to 1° C., this value being taken from the reductions by Regnault's*

formula as being probably more accurate than those made by Bosscha's alleged corrected formula.

32. A number of observations, the details of which are given in Part II., show that, admitting the accuracy of Latimer Clark's valuation of the E.M.F. of his standard cell (Proc. Roy. Soc. 1872, vol. xx. p. 444) as being 1.457×10^8 C.G.S. units at 15° , the value of e in the expression $e = E - H\chi J$ (§ 11) is 1.5003×10^8 C.G.S. units when water is electrolyzed at a temperature of 15° – 20° , the value of J being taken as 42×10^6 —the probable error of the mean result being ± 0.0048 , or ± 0.32 per cent. Owing, however, to certain causes detailed in Part II. (§ 39), this value is slightly too low—this result being essentially due to the impracticability of collecting every trace of gas evolved, so that the value of H (the heat evolved per gramme-equivalent of water decomposed) is slightly overvalued, and hence e slightly undervalued.

From the combustion experiments of previous investigators, summarized in the preceding eight paragraphs, it results that the value of e in the expression $e = H'\chi J$ (§ 11) is 1.5038×10^8 (since $H' = 34,100$), J being, as before, taken as 42×10^6 . These numbers, 1.5003×10^8 and 1.5038×10^8 , accord so closely as to show that (so far as these experiments can decide) the value of J cannot be far from 42×10^6 . Applying the formula

$$J = \frac{E}{(H + H')\chi}$$

(§ 24) to the experimental data given in Part II., the average value deduced for J is 41.96×10^6 , this value for J giving the following values for e :—

$$\begin{array}{llll} \text{From formula } e = E - H\chi J & . & . & e = 1.5023 \times 10^8 \\ \text{,,} & \text{,,} & e = H'\chi J & . & . & . & e = 1.5024 \times 10^8. \end{array}$$

Since, however, the mean value of H is slightly overvalued, it results that the value of J finally deduced is slightly *above* 41.96×10^6 , with a probable error of less than ± 0.4 per cent., *i. e.* of less than $\pm 0.016 \times 10^6$, due to the electrolytic experiments, the probable error in the determination of H' not being taken into account.

33. It is evident that, considering the nature of the data from which this conclusion is drawn, not much dependence

can be placed on the final value of J deduced except as an approximation. It is noteworthy, however, that this value of J very closely agrees with that deduced by Joule in 1867 (B. A. Reports, 1867), by determining the heat producible in a wire of known resistance by a known current, and that both are perceptibly higher than the value obtained by Joule by means of water-friction &c. in 1850 (Phil. Trans. 1850, p. 61); whilst this older value is completely corroborated by his recently made experiments on water-friction &c. (Phil. Trans. 1878, p. 365). In 1850 Joule found that the heat required to raise 1 lb. of water (weighed *in vacuo*) from t to $t+1$ (where t lies between 55° and 60° F.) corresponded to the following number of foot-pounds at Manchester:—

By friction of water	. . .	772·692
„ „ mercury	. .	774·083
„ „ cast iron	. .	774·987

Of these values the first was considered probably the most accurate; and as a little vibration and sound was unavoidable in the experiments, the round number 772 was adopted as the most probable value. The 1878 value finally arrived at is that the heat required to raise 1 lb. of water (weighed *in vacuo*) from 60° to 61° F. corresponds to 772·55 foot-pounds, and is hence sensibly identical with the former result. The 1867 values, however, were as follows, expressed in foot-grain-second units:—

			Per grain degree F. (water weighed in air).
1st series.	Mean of 10 experiments	. .	25335
2nd „	„ 15 „	. .	25366
3rd „	„ 30 „	. .	25217

Of these the last value was taken as most exact; when reduced to water weighed *in vacuo* it becomes 25187. As in this series the average temperature of the calorimeter was $18^{\circ}·63$ C. = $65^{\circ}·5$ F., the final result is that, to raise the temperature of 1 gramme of water from 65° to 66° F., requires 25,187 foot-grain-second units of work.

34. When reduced to C.G.S. measure and degrees Centigrade the three values, 772·692 foot-pounds, 772·55 foot-pounds, and 25,187 foot-grain-second work units, become respectively 41·60, 41·59, and 42·14 megalergs per gramme-

degree, the value of g at Manchester being taken at 981.3. (Compare illustrations of the C.G.S. system of units, by Prof. Everett, p. 51.) Since, however, the specific heat of the water at the three assigned temperature-limits, 55°–60°, 60°–61°, and 65°–66° F., is not quite the same, on reduction to the gramme-degree taken above as unit (the heat requisite to raise 1 gramme of water from 0° to 1° C.), these values become

$$\frac{41.60}{1.0008} = 41.57, \quad \frac{41.59}{1.0009} = 41.54, \quad \text{and} \quad \frac{42.14}{1.0010} = 42.10$$

megalergs respectively when Regnault's formula for the specific heat of water (§ 25) is taken; whence the mean value of J is 41.555 megalergs from the two sets of friction experiments (1850 and 1878), and 42.10 by the electric-current method (1867)—the latter consequently being $\frac{42.10}{41.555} = 1.0131$ times the former, or 1.31 per cent. in excess. The value for J deduced above from the writer's experiments (viz. 41.96 megalergs) is $\frac{41.96}{41.555} = 1.0098$ times that got from Joule's friction experiments, showing an excess of 0.98 per cent. Hence, on the whole, the writer's numbers and Joule's 1867 values concord much more exactly than might have been anticipated, each showing an excess over Joule's water-friction value (1850 and 1878) of about 1 per cent., Regnault's formula being employed for reducing the observed rise of temperature to gramme-degrees at 0°–1° C.

35. Reasons have already been given (§ 32, *vide* also Part II. § 39) for supposing that the value 1.5003 found for the E.M.F. representing the affinity for oxygen and hydrogen in water is slightly understated. The effect of an error of this kind would be to raise the value of J deduced by the formula

$$J = \frac{E}{(H + h)\chi} \quad (\S 24),$$

and hence to make the excess of the value of J thus deduced over Joule's water-friction value to be somewhat more than the 1 per cent. or thereabouts just calculated. It is worthy of notice that there is also reason for supposing that Joule's 1867 value is understated. Experiments are described in Part II. the result of which is to show that an unobserved source of

error existed in Joule's 1867 experiments, the effect of which was to diminish the value of J thence deduced by an amount probably equal to some tenths per cent.; so that on the whole Joule's 1867 value, when corrected, is probably from 1.5 to 2.0 per cent. higher than his water-friction value (1850 and 1878).

This difference between the two values is precisely that which would subsist did an error to an equal amount exist in the B.A. resistance-unit valuation: *i. e.* if the B.A. unit were 1.015 to 1.020 earth-quadrant per second instead of being exactly 1 earth-quadrant per second, the value of J deduced from Joule's 1867 experiments would be 1.015 to 1.020 times the true value; for it is calculated by the formula

$$J = \frac{C^2 R t}{H},$$

where C is the current, R the resistance, t the time, and H the heat evolved. Moreover the existence of such an error in the B.A. unit would cause a precisely corresponding error in Latimer Clark's valuation of the E.M.F. of his standard cell (Proc. Roy. Soc. 1872, vol. xx. p. 444), this valuation being based on the determination of the resistance R between two points traversed by a known current C , the potential difference E between the points being equal to the E.M.F. of the cell, so that by Ohm's law $E = CR$; and the effect of this would be to cause a precisely similar error in the value of J deduced by the formula $J = \frac{E}{(H + h)\chi}$, as in the writer's experiments.

36. In confirmation of the supposition that the B.A. unit of resistance is too large, Kohlrausch's experiments may be cited (Phil. Mag. 1874, vol. xlvii. pp. 294 & 342). A careful comparison of several copies of the B.A. unit with coils standardized by himself in absolute measure led Kohlrausch to the conclusion that the B.A. unit is really 1.0196 earth-quadrant per second, or 1.96 per cent. too large; for he found that the resistance of certain coils graduated in Siemens mercury units averaged 0.9717×10^9 C.G.S. units, whilst the B.A.-unit coils averaged 1.0493 times the resistance of the Siemens coils, giving therefore for the B.A. unit the value

$$0.9717 \times 1.0493 \times 10^9 = 1.0196 \times 10^9.$$

On the other hand, it is to be observed that Lorenz has

made a determination of the value of a Siemens mercury unit with a lower result (*Pogg. Ann.* 1873, vol. cxlix. p. 251), viz. 0·9337 earth-quadrant per second. Lorenz's mercury-tubes were made by himself; and it does not seem from his paper that any evidence was obtained of the purity of the mercury used other than the fact that its specific gravity at 5°·3 C. was 13·586 after digesting for a long time with nitric acid. These mercury-tubes do not seem to have been compared directly with any B.A.-unit coil so as to give the value of the B.A. unit in absolute measure; on comparing them with a reputed Siemens unit, Lorenz found a difference of nearly 1 per cent. ($0\cdot943 \times 10^9$ as against $0\cdot9337 \times 10^9$)—the difference between Lorenz's mercury-tube value of a Siemens unit and the value of the latter in B.A. units, as deduced by Kohlrausch, being nearly exactly double this amount, or nearly 2 per cent., $\frac{1}{1\cdot0493} \times 10^9 = 0\cdot9530 \times 10^9$ as against $0\cdot9337 \times 10^9$.

37. Yet, again, values for J have been obtained by other observers considerably higher than that deduced from Joule's water-friction experiments. The following Table (mainly taken from Prof. G. C. Foster's article "Heat" in Watts's 'Dictionary of Chemistry,' 1st Supplement, p. 687) gives the chief of these results expressed in gravitation measure, no corrections being made for differences in the value of *g* at the various localities where the experiments were made, or in the specific heat of water at different temperatures. The last column gives the approximate ratio of the value found to that deduced by Joule from water friction, this latter being taken as 423·5 metre-grammes per gramme-degree Centigrade:—

Observer.	Method employed.	Value of J found.	Ratio to Joule's water-friction value.
Hirn	Crushing of lead	425·2	1·004
"	Friction of water and brass.....	432	1·020
"	Escape of water under pressure	433	1·023
"	Specific heats of air	441·6	1·043
Joule	Heat produced by electric currents	429·3	1·014
Violle.....	" " induced currents (aluminium)	434·9	1·027
"	" " " " (copper) ..	435·2	1·028
"	" " " " (tin)	435·8	1·029
"	" " " " (lead)	437·4	1·033
Regnault...	Velocity of sound	437	1·032

On the whole, it is evident that further experiments are desirable as to the development of heat in circuits of resistance measured in terms of the B.A. unit by known currents, so as to establish as accurately as possible a connexion between the values of J and of the B.A. unit, so that if the first is assumed to be correctly given by Joule's water-friction value the error (if any) in the B.A. unit can be calculated, or so that the value of J can be determined afresh when the precise value of the B.A. unit is known from further experiments. The writer hopes shortly to be enabled to communicate the results of experiments in this direction made by a method differing from that employed by Joule in certain important points, so as to avoid the sources of error existent in Joule's 1867 experiments (Part II.).

PART II.—*By* Dr. C. R. ALDER WRIGHT *and* E. H. RENNIE, *M.A. (Syd.), B.Sc. (Lond.), Demonstrator of Chemistry in St. Mary's Hospital Medical School.*

Experimental Determination of the Electromotive Force corresponding to the Work done in the Decomposition of Water into Oxygen and Hydrogen at the ordinary temperature.

38. In order to apply the principles described in Part I. (§§ 11, 18, 32), the current from a Daniell battery was passed through a voltameter placed in a calorimeter, and the average difference of potential between the voltameter-plates determined by connecting them with a quadrant electrometer standardized by a Clark cell (verified for us by Dr. Alexander Muirhead). The amount of decomposition being determined ($=n$ grammes), and the quantity of heat, h , developed in the voltameter observed, the data were obtained for the calculation of the E.M.F. representing the nett work corresponding to the sum of the physical and chemical changes taking place by the formula

$$e = E - \frac{ha\chi J}{n},$$

a being the equivalent of the electrolyte.

In the case of water acidulated with sulphuric acid, the following results were obtained. The voltameter consisted of