IX. *The Latent Heat of Evaporation of Water.*

By E. H. GRIFFITHS, *M.A.*, *Sidney Sussex College, Cambridge.*

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[PLATES 4–6.]

CONTENTS.

Section I.—INTRODUCTORY NOTE.

IT is possible that I have in succeeding pages, when describing apparatus and methods of observation, entered unnecessarily into matters of detail. In defence, I would urge that the accuracy of determinations of physical constants depends on the amount of attention devoted to apparently trivial matters, and that in the absence of full information, it is impossible to rightly estimate the value of the results. Corrections are often rendered necessary by subsequent re-determinations of the constants involved, and the application of such corrections is only possible when the writer has given his data in full. Much valuable experimental work has with lapse of time become useless, owing to the author's natural reluctance to overcrowd his communication with details which may at the time very possibly appear both unnecessary and trivial.

Although the experiments described in this paper were not commenced until the Summer of last year (1894), the preparation of the apparatus and the standardisation of the instruments has engaged my attention for a considerable time. Nearly the whole of the Spring and Summer of 1893 were expended in fruitless efforts to render the calorimeter and its connections absolutely air-tight, and I found it impossible to secure perfection in this respect until in the Autumn of that year I succeeded in obtaining an alloy, by means of which I was able to unite glass and metal tubes in a satisfactory manner. The calorimeter and connections had then to be practically reconstructed and some improvements added, which experience had shown to be desirable.

My original intention was to conclude my investigations into the latent heat of evaporation of water over the range 10° to 60° C. before publishing my results, and, had it not been for two misfortunes, I think that I should have now completed the necessary experiments. An accident to the apparatus early in September involved a loss of about ten days, and also compelled a redetermination of the capacity for heat of the calorimeter. A second mischance was a temporary break-down in my health, which compelled me to be absent from my laboratory for some days, and on resuming the work I was at first able to devote but little energy to it. During the University Term my time is not my own, and hence, when October 13 found the inquiry unfinished, I was compelled to relinquish all hopes of completing my original scheme until the Long Vacation of 1895 should again provide me with the necessary leisure.

I feel, however, that all the experimental difficulties have been overcome, and I regard the work as completed at certain temperatures. I do not propose to repeat the observations at those temperatures, and therefore I see no necessity to defer the publication of the results for another twelve months.

Again, the facts set forth in Section XI. appear to me to so strengthen the conclusions to which my experiments have led me as to render any postponement unnecessary.

I wish to express my sincere thanks to Mr. C. T. HEYCOCK and Mr. F. H. NEVILLE for many valuable suggestions, and also for their help with the experiments on certain critical occasions.

During the summer of 1893 I was assisted by Mr. G. M. CLARK, B.A., and throughout 1894 by Mr. C. GREEN, Scholar of Sidney Sussex College, and I am glad to have this opportunity of acknowledging my indebtedness to both those gentlemen.

As frequent references have to be given to two former papers, I denote them as follows :—

Paper J." "The Mechanical Equivalent of Heat," 'Phil. Trans.,' vol. 184 (1893), A, pp. 361–504.

Paper A." "The Influence of Temperature upon the Specific Heat of Aniline," 'Phil. Mag.,' January, 1895.

Section II.—HISTORICAL.

The following is, I think, a fairly complete table of results published since the year 1843 :—

TABLE I.

Temperature.	Observer.	No. of experiments.	Extreme values for L.	Mean L.†	Reference.
0°	DIETERICI . .	20	595·52–598·84	596·8	'Wied. Ann.,' vol. 37, 1889
− 2° to + 16°	REGNAULT . .	22	..	..	'Mémoir. de l'Acad.,' vol. 21, 1847
63°–88°	" . .	23	..	..	" " "
99°·88	" . .	44	533·3–538·4	536·67	" " "
99°·81	FAVRE and SILBERMANN	3	532·59–541·77	535·77	'Ann. de Chimie,' vol. 37, 1853
100°	ANDREWS . .	8	530·8–543·4	535·9	'Chem. Soc. Journ.,' 1849
100°	BERTHELOT .	3	535·2–537·2	536·2	'Comptes Rendus,' vol. 85, 1877
100°	SCHALL . . .	No de	tails given	532·0	'Ber. d. Chem. Ges.,' vol. 17, 1884
100°·16	HARTOG and HARKER*	5	523·61–525·87	524·60	'Manchester Phil. Soc. Proc.,' 1893–4
119°–194°	REGNAULT . .	73	..	..	'Mémoir. de l'Acad.,' vol. 21, 1847

The values obtained by WINKELMANN ('Wied. Ann.,' vol. 9, 1880) are not included in the above table, as they are not based on independent experiments, but deduced from the observations of REGNAULT.

I do not propose to examine at length any of the above determinations except those

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[*] It is right to add that Messrs. HARTOG and HARKER state that these are the results of "Preliminary Experiments," and should not be regarded as giving their final conclusions. I do not, therefore, include their work in my criticisms.

[†] It must be remembered that all the above values of L (with the exception of DIETERICI'S) depend upon some assumption as to the changes in the specific heat of water caused by changes in temperature, for they are either deduced from "the total heat of steam," or depend upon the observation of the rise or fall in temperature of a certain mass of water. Again, as the nature of the thermal unit adopted by the observer is, in some cases, doubtful, an uncertainty of an order of about 1 per cent. is thus introduced.

by REGNAULT and DIETERICI, for none of the other observers appear to me to have devoted as much care and attention to the matter. In some cases, *e.g.*, ANDREWS and BERTHELOT, we have records of only a few observations evidently undertaken not so much with the object of obtaining an accurate determination of the latent heat of evaporation of water, but rather for purposes of comparison with other liquids. In other cases there are not sufficient details as to the thermometry, the unit of heat adopted, &c., to render a close criticism of any profit.

Again, DIETERICI is the only observer who has made direct experiments at temperature 0° C. REGNAULT's observations extended from 63° to nearly 200° C., and he also performed a number of experiments where the temperature of the vapour was between $-2°$ and $+16°$, although this last group must be regarded (and I think was regarded by REGNAULT himself) as of less value than his observations at higher temperatures.

The method employed by DIETERICI was in principle very similar to that adopted by me and described in subsequent pages.*

The heat required for the evaporation was abstracted from water at 0° and the amount of heat deduced from the quantity of ice formed. The advantages of such a method (upon which I shall more fully dwell when I describe my own work) are as follows:—

(1.) No change of temperature takes place, thus all difficulties connected with the capacity for heat of the apparatus and its contents are avoided.

(2.) The observer is almost entirely independent of thermometry—an advantage which, to my mind, it is almost impossible to overestimate.

DIETERICI's experimental results, as stated in Table I. (*supra*), vary from 595·52 to 598·84, but it should be noticed that both these extremes occur in his Table I. He afterwards made what he considered to be improvements in the apparatus, and the extreme values of his last 13 experiments (see his Tables II., III., IV.) are 595·74 and 597·29. His mean result is 596·80, and I would particularly draw attention to his last two experiments, where he very greatly increased the rapidity of evaporation by suddenly opening the communication between his evaporating vessel and a condenser containing sulphuric acid in which the pressure was reduced as far as possible by means of a mercury pump. These two experiments give respectively 597·07 and 596·68. The agreement between the individual experiments throughout the whole series leaves little to be desired, and, if it were not for one doubt, I would without hesitation accept those results as conclusive; but I am afraid, for the following reasons, that our knowledge is not yet sufficiently exact.

The quantities of heat were deduced by measuring the mass of mercury expelled from the BUNSEN calorimeter during the formation of ice, and the results, therefore,

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* My own experiments described in this paper were completed before the work of DIETERICI came to my notice, and the close similarity between the general principles adopted by both of us is a matter of chance, not of design. Had I previously perused his paper, I should have been saved much time and many preliminary experiments.

depend entirely on the constant which gives the relation between the quantity of heat and the mass of expelled mercury. DIETERICI in this matter shifts the responsibility on to other shoulders. His only reference to the subject is as follows:—

"Diese sind gemessen in mittleren Calorien, also in dem hundertsten Theile derjenigen Wärmemenge, welche ein Gramm Wasser von 0° auf 100° erwärmt, und zwar liegt der Berechnung der Mittelwerth der Beobachtungen von BUNSEN, SCHULLER und WARTHA und VELTEN,[*] zu Grunde dass einer mittleren Calorie 15·44 mg. Hg. entsprechen."[†]

Now, BUNSEN by assuming his own value of this constant obtained 80·025 as the latent heat of fusion of ice, and the marked difference between this number and that obtained by REGNAULT (79·24), requires explanation. This discrepancy is greater than appears at first sight, for the "mean thermal unit" (over the range 100° to 0°) adopted by BUNSEN is supposed to be greater than the "thermal unit at 15°" adopted by REGNAULT during his researches into Latent Heat, and thus the divergence would be increased if both were expressed in terms of the same thermal unit.

The doubt introduced by the above considerations is due to uncertainty regarding the comparative magnitude of the different thermal units and does not affect the value of DIETERICI'S experiments, although it renders his conclusions somewhat uncertain.

There can be but little doubt that the mass of mercury expelled from a Bunsen calorimeter by the subtraction of a definite thermal unit is a quantity that can be, and doubtless will be, determined with accuracy, and if any correction on the conclusions arrived at by BUNSEN, SCHULLER and WARTHA, and VELTEN is found to be necessary, it can be applied to the values of the latent heat of evaporation at 0° obtained by DIETERICI.

This case well illustrates a matter to which I have before endeavoured to call attention,[‡] viz., that a mistake in thermometry is a fatal error in experimental work. It is impossible to correct the conclusions arrived at by the investigator, however our knowledge of thermometry may increase, since we should require to have in our possession the actual thermometer used by the observer, together with a full knowledge of the circumstances under which it was observed. As before remarked, DIETERICI'S results were independent of thermometry, hence their peculiar value.

REGNAULT'S formula for the "total heat of steam" has been so generally accepted, and the experiments upon which he founded it are so justly considered as examples of that singular skill and ability for which all his work is distinguished, that it is with diffidence that I venture to offer criticisms on his methods or conclusions. I would repeat that REGNAULT himself evidently attached less importance to his determina-

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[*] The actual values obtained by these observers were as follows:—BUNSEN, 15·41; SCHULLER and WARTHA, 15·442; VELTEN, 15·47 mg. 'Wied. Ann.,' vol. 33, 1888, p. 439.

[†] 'Wied. Ann.,' vol. 37, 1889, p. 499.

[‡] 'Science Progress,' April, 1894.

tions at low temperatures than to those above 65° C. In Table IV. of his paper, "Sur les chaleurs latentes de la vapeur aqueuse à saturation sous diverses pressions," are given the results of all his experiments below 63°, and in his introductory remarks to this table (pp. 712–719) he clearly indicates his comparative want of confidence in the results.*

A searching criticism of REGNAULT's work is given by WINKELMANN in 'Wied. Ann.,' vol. 9, 1880, and had the limits of this communication permitted it, I should have liked to quote several pages of that paper, but I will content myself with giving a short summary of his arguments.

I would first remark that WINKELMANN's object was to explain the discrepancy between what he terms the "theoretical density" of water vapour, and that which results from "the mechanical theory of heat." He assumes the former as 0·6225; but does not give the data by which he obtains that number (I find that if we take the molecular weight of H_2O as 17·98, and the density of H as ·06924 (air = 1), we arrive at the same value). He then (assuming that J = 424) calculates the density from the thermodynamic equation $L = T/J\ (s' - s)\ dP/dT$, by substituting for L—

(*a*) the values resulting from REGNAULT's formula for the "total heat," viz.,

$$606{\cdot}5 + {\cdot}305t,$$

(*b*) the values of L given by the equation

$$L = 589{\cdot}5 - 0{\cdot}2972t - 0{\cdot}0032147t^2 + 0{\cdot}000008147t^3. \quad . \quad . \quad . \quad (W),$$

the last being a formula constructed by WINKELMANN, but based on REGNAULT's experiments at high temperatures.

WINKELMANN contends that not only does the use of (W) bring the values obtained by the "mechanical theory" into greater harmony with the "theoretical value," but also that the formula (W) is in closer agreement with REGNAULT's experiments than is the formula given by REGNAULT himself.

True, the values obtained by WINKELMANN are always greater than 0·6225, but he contends that it is impossible to imagine the real density as less than the "theoretical," although it is easy to see that it may be greater.

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[*] "J'ai cherché à obtenir la chaleur latente de la vapeur d'eau à saturation aux basses températures par une autre méthode qui me permettra, j'espère, d'obtenir cette donnée avec beaucoup d'exactitude et contre laquelle on ne peut pas élever les objections que nous avons faites contre le premier procédé. Mais cette méthode, que j'ai décrite à la fin de mon Mémoire sur l'hygrométrie ('Annales de Chimie et de Physique,' 3e série, tome 15, p. 227), exige la connaissance de plusieurs données sur lesquelles il reste encore beaucoup d'incertitude. On a besoin notamment de connaître la capacité calorifique de l'air et la quantité de chaleur que l'air absorbe pendant sa dilatation. Il m'a paru nécessaire de déterminer ces deux éléments par de nouvelles expériences, et c'est seulement lorsque celles-ci seront terminées que je pourrai calculer les déterminations de la chaleur latente de la vapeur d'eau," p. 722.

When I give the results of my experiments, I think that I shall be able to show that WINKELMANN in his desire to lower the value of L at low temperatures has considerably overshot the mark, and that in deducing the values at, or near, 0° from experiments above 65° he has carried the method of extrapolation beyond due bounds. At present, however, I will only consider his reasons, with which I agree in the main, for rejecting REGNAULT's determinations at lower temperatures.

(1) There is no doubt that REGNAULT's formula does not give the mean result of his experiments at low temperatures. In all, he performed twenty-two experiments at temperatures below 65° (Table IV., 'Mémoir. de l'Acad.,' xxi., 1847), and the mean value given by these twenty-two experiments differs from that given by his formula by 1·8.

(2) The experiments above referred to were performed in a different manner from those at the higher temperatures. The water to be evaporated was placed in a spiral within the calorimeter, and the pressure reduced until the water boiled, the vapour being condensed in a vessel surrounded by ice. REGNAULT deduced the temperature of the water when evaporating by observing the pressure of the vapour in the condenser—hence, as REGNAULT himself says, "It is probable that the elastic force observed on the barometric manometer is decidedly less than the mean pressure at which the vapour is distilled," and thus the evaporation is taking place under a greater pressure and at a higher temperature than that given by his Table IV.

Again, the temperature of the saturated vapour is sensibly beneath the temperature of the calorimeter, and so lowers the temperature of the calorimeter more than would be done by the evaporation alone.

In the case of other liquids, REGNAULT made a correction for the heat abstracted by the vapour while passing out of the calorimeter, but he did not apply this correction in the case of water. It is true that no special arrangements were made to warm the vapour to the calorimetric temperature (as was done by coils with the vapours of other liquids), but there can be no doubt that the vapour must have abstracted heat from the walls of the calorimeter.

Let k be the specific heat of the vapour, t the temperature at which evaporation takes place, t_0 and t_1 the initial and final temperatures of the calorimeter, then the heat per unit mass absorbed should be $k\{\frac{1}{2}(t_0 + t_1) - t\}$; at the same time this is not a correction that can be applied with certainty.

(3) At these low temperatures a small difference in the pressure of the vapour corresponds to a considerable difference in temperature; thus, if the temperature of the water is deduced from the pressure in the receiver, the error may be considerable.* The effect of all these errors would be to make the value of L given by REGNAULT's experiments too great.

The above criticisms do not apply to the experiments at the higher temperatures.

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* For example, a difference of 0·4 millim. at 4° would correspond to a difference of 1° C.

I think the preceding summary fairly represents the remarks of WINKELMANN on the determinations at low temperatures.*

I will now add some remarks of my own.

REGNAULT was compelled to limit the duration of these experiments as much as possible, otherwise his correction for the loss or gain by radiation, etc. (which was at best but a somewhat uncertain one) became large as compared with the other magnitudes to be measured. The average length of an experiment was about five minutes, though in one or two extreme cases it extended to 11 minutes; in this time he evaporated about 5·3 grams of water, and thus he was compelled to reduce the pressure in the condenser very considerably below the pressure of saturated vapour at the temperature of the calorimeter. He was, therefore, unable to diminish the sources of error (subsequently dwelt upon by WINKELMANN) in the manner he might have done had he not been thus limited in time. REGNAULT, referring to the difference between the pressure in the condenser and in the calorimeter, writes as follows: "La différence entre les deux tensions doit même être assez grande; car pour que l'expérience se fasse dans des conditions favorables d'exactitude; il faut que la distillation soit assez rapide, afin que la correction *e* ne soit jamais qu'une fraction très-petite de $t_0 - t_1$."†

Again, another matter of importance is the thermometry. On p. 692 (*ibid.*) he says: "Les thermomètres à mercure des calorimètres ont étés gradués avec le plus grand soin, un degré centigrade occupe sur la tige du thermomètre

du calorimètre C. . . . . 18°·7620; par suite 1° vaut 0°·053283.
„ C′. . . . . 18°·5800; „ 1° „ 0°·053821.

Il est facile d'apprécier avec certitude le dixième des divisions, c'est-à-dire $\frac{1}{200}$ de degré centigrade dans les lunettes horizontales avec lesquelles on observe les thermomètres."

The only other reference is on p. 707, where he remarks that he reduced the readings from the mercury to the air scale by means of the table given on p. 239 of his paper "De la mesure des Températures."‡ I have searched the paper throughout for some indication as to the thermometers actually used, in the hope that I might be able to identify them with some one of those of whose comparison with the air thermometer he gave an account in another paper; but the above are the only references to the thermometry that I have been able to find. Had a direct comparison between these thermometers and the air thermometer been made, it is most probable that REGNAULT would have mentioned it; we may, therefore, assume that,

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* Had not REGNAULT measured the temperature of the evaporating water by means of the vapour pressure in the condenser, the above objections would lose their force.

† 'Mémoir. de l'Acad.,' vol. 21, 1847, p. 716.

‡ 'Mémoir. de l'Institut,' vol. 21, p. 220

knowing the nature of the glass, he simply reduced them to the air scale by the table above referred to.

Throughout the low temperature determinations the temperature of the calorimeter fell during an experiment through about 5°·6 (in the greatest case 5°·761), and thus an error of 0°·01 in his thermometry would cause a difference of more than 1 in 600 in the results. At higher temperatures, however, the average rise in the temperature of the calorimeter exceeded 12° and thus the effect of any such thermometric error would be considerably reduced.

Again, the observations of the change in temperature of the calorimeter at low temperatures were always taken on a falling thermometer. I have in a previous paper (J., p. 442) expressed my disbelief in the value of any observations of mercury thermometers when their temperature is falling. I am not alone in this opinion,* and it has been confirmed by subsequent experience. I am sure that inaccuracies of a much larger order than 0°·01 would have presented themselves from this cause alone, and the great divergences observable amongst REGNAULT's individual experiments at low temperatures is I have no doubt partly attributable to this cause.† In all his experiments at higher temperatures, however, his thermometers were rising and the discrepancies between individual observations were much less marked.

It will be noticed that the various sources of error which have been enumerated either disappear or are much diminished at the higher temperatures.

Again, the ever-recurring difficulty with regard to the specific heat of water presents itself. The correction is not so simple as has been assumed by those who have merely applied REGNAULT's own formula for the specific heat of water to the expression for the total heat of steam, for the correction would have to be applied during the reduction of each separate experiment, as the quantity of heat absorbed by the calorimeter and contents when warming or cooling through a degree of temperature would vary according to the mean temperature of the range and the resulting correction would, I believe, be greater than is usually supposed.

There appears to be but little doubt that REGNAULT's expression for the changes in the specific heat of water is inaccurate. As far as I know, ROWLAND (1877), BARTOLI and STRACCIATI (1889), and myself (1892) are the only observers who have seriously attacked this difficulty since the time of REGNAULT, and all agree in one conclusion, viz., that the specific heat of water diminishes as the temperature rises to 20°, and the methods of experiment employed by these observers were so entirely different that their agreement in this matter carries great weight. We cannot, therefore, accept without question REGNAULT's conclusions as to the changes at higher temperatures. The magnitude of the correction involved may be illustrated, as pointed out by DIETERICI himself, by the following example. If we assume

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* SCHUSTER and GANNON, Communication to the Royal Society, Nov. 22, 1894.

† The comparatively slow rate of stirring would also tend to make the temperature measurements uncertain.

ROWLAND'S value for the specific heat of water at 15° C., the difference between the thermal unit at 15° C. and "the mean thermal unit" over the range 100° to 0°, amounts (if we accept DIETERICI'S interpretation of REGNAULT'S values) to nearly $1\frac{1}{2}$ per cent.,* and would reduce the value of L at 0°, as given by REGNAULT'S formula (viz., 606·5), *below* the value found by DIETERICI (598·8).†

The tacit assumption amongst physicists that the discrepancies arising from doubts as to the value of the thermal unit are so trivial that they may be disregarded is, as shown by the above example, much to be regretted, and the many efforts to deduce specific volumes, etc., from the equation $J = L/T\,(s' - s)\,dp/dT$, shows how frequently this difficulty is ignored. It is strange that, although so much attention has been devoted, during recent years, to the exact determination of various physical units, so little has been done with regard to this extremely important fundamental constant.

The experimental difficulties are not so great as to prevent all progress, and I venture to appeal to the Royal Society to consider this matter; indeed, I would go so far as to express my personal belief that the method of measuring small differences of temperature indicated in a paper read before the Physical Society last October removes many of the difficulties which have hitherto barred the way.

It is, I think, evident that we are not justified in concluding that our knowledge of the value of the latent heat of evaporation of water at low temperatures is sufficient. It has been already shown that the effect of most of the causes of error above enumerated diminishes at higher temperatures; and a study of REGNAULT'S Tables I. to III. will confirm the conclusion that we may regard the results at those temperatures as of greater accuracy. Even at higher temperatures, however, the difficulties with regard to the measurement of differences of temperature and of the capacity for heat of water present themselves.

I can find no record of experiments by any observer at temperatures between 16° and 65° C.

The above considerations are, I think, sufficient to indicate the necessity of a re-determination of the latent heat of evaporation of water, at all events at low temperatures.

Section III.—DESCRIPTION OF THE METHOD.

I was anxious, if possible, to devise a method of such a nature that my results would not be appreciably affected by

(1) errors in thermometry,
(2) changes in the specific heat of water,
(3) the capacity for heat of the calorimeter,
(4) loss or gain of heat by radiation, &c.,

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* At the end of this paper I give figures which lead to the conclusion that the difference between the "mean thermal unit" and the "thermal unit at 15°" is less than is usually assumed.

† DIETERICI, 'Wied. Ann.,' vol. 37, 1889, p. 506.

and if these points are borne in mind they may serve to explain some of the contrivances which might otherwise appear uncalled for.

If the vessel in which the evaporation is taking place is kept at a constant temperature, we are independent of the capacity for heat of it and its contents; we also dispense with the measurements of changes of temperature. Thus, if matters be so arranged that the loss and gain of heat throughout an experiment are balanced, many fruitful causes of error are avoided. Of course, the actual temperature of the calorimeter during evaporation must be determined, but a small error here is of little consequence. The change in the value of L (when L is the latent heat of evaporation of water) is small as compared with the changes in θ. In fact, an accuracy of an order of $\frac{1}{10}$ of a degree would be sufficient when determining the actual elevation.

The heat was supplied to the calorimeter by means of a wire whose ends were kept at a constant potential difference. The thermal balance could be maintained in one of two ways,

(1) If the heat supply was too great, the electric current could be temporarily stopped: or, the rate of evaporation of the water increased. (The latter was the method that I generally adopted.)

(2) If the cooling was too rapid, the only mode of maintaining the balance was (in the apparatus about to be described) to reduce the rate of evaporation.

The water to be evaporated was placed in a small silver flask, connected with which was a spiral coil of silver tubing 18 feet in length. Both flask and spiral were within the calorimeter, and the water-vapour, after passing through the spiral, emerged from the apparatus at the temperature of the calorimeter. Surrounding the flask, and between it and the spiral, a coil of platinum silver wire was arranged, and flask, spiral and coil were entirely immersed, in aniline during my preliminary experiments, subsequently in a certain oil of which an account will be given later.

The calorimeter (which was filled to the roof with the aniline or oil, and the equality of temperature maintained by rapid stirring) was suspended by glass tubes within a steel chamber, whose walls were maintained at a constant temperature. So long, therefore, as the calorimeter and the surrounding walls were at equal temperatures, there was no loss or gain by radiation, &c. If during an experiment the temperature of the surrounding walls changed, the method of experiment involved a corresponding change in the temperature of the calorimeter, and, therefore, some loss or gain of heat would be experienced. The apparatus was so designed that any such change in temperature was extremely small (in no case amounting to $\frac{1}{100}°$), yet, in order to estimate the loss or gain, it was necessary to know approximately the capacity for heat of the calorimeter and contents.

Small differences between the temperature of the calorimeter and the surrounding walls would, during an experiment, be of no consequence, provided that the oscillations were of such a nature that the mean temperature of the calorimeter was that of the surrounding space, and I think I shall be able to show that this condition was fulfilled.

In addition to the heat supplied by the electric current there is also a supply due to the work done by the stirrer. It was in the estimation of this "stirring supply" that I found my greatest difficulties, and I regard that portion of my determinations with the least confidence. Fortunately the heat thus generated was only about $\frac{1}{100}$ of the heat supplied by the current, and thus any small error in that portion of the work becomes of little account.

Of the accuracy with which the electrical supply could be measured, there is no question, and I have but one remark to make on this portion of the subject, viz., that even if the values of the E.M.F. of my Clark cells, or the absolute resistance of the box-coils given by the standardisations performed during my determinations of J, are in any way inaccurate, such errors would eliminate, since the value of J was determined by means of the same standards as those by which the quantity of heat developed in these experiments was determined. Hence, by assuming my former value of J, I get the comparison in terms of a thermal unit at 15° C., independently of the numerical value of J assumed in the reductions.

One further correction remains to be noticed. I have spoken of the temperature of the calorimeter as oscillating about the exterior temperature, and it might happen that at the close of an experiment this difference was not the same as that at the commencement—if any such difference existed. The magnitude of this correction depended, of course, on the ability of the observer to maintain the thermal balance. In these experiments the correction was extremely small, and in any case could be determined with great accuracy.

Having indicated the nature of the observations I will proceed to state the relation between the various sources of loss, or gain of heat.

Let Q_e be the thermal units per second due to the electrical supply.
,, Q_s ,, ,, ,, ,, ,, mechanical supply.
,, Σq be the total heat supply during an experiment from any other causes.

Then, if M be the mass of water evaporated, L the latent heat of evaporation at temperature θ, and if the electrical supply is maintained for a time t_e, and the mechanical for a time t_s,

$$\mathrm{ML} = \mathrm{Q}_e t_e + \mathrm{Q}_s t_s + \Sigma q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

Now the D.P. at the ends of the coil was always some integral multiple of the D.P. of a Clark cell.

Let e be the D.P. of a Clark cell, n the number of cells, and R_1 the resistance of the coil at the temperature θ_1, then

$$\mathrm{Q}_e = \frac{e^2 n^2}{\mathrm{R}_1 \mathrm{J}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

If the calorimeter at the commencement and end of an experiment was at exactly the same temperature as the surrounding walls, then if their temperature was unchanged, the term Σq would vanish; but although this term throughout these experiments was of small dimensions, it could not be entirely ignored.

Let θ'_0 and θ''_0 be the temperature of the surrounding walls at the beginning and end of an experiment; suppose the calorimeter temperature (θ_1) to exceed the surrounding temperature by d' at the commencement and d'' at the end of an experiment. Then fall in temperature of calorimeter

$$= (\theta'_0 + d') - (\theta''_0 + d'').$$

Hence the heat given out by the calorimeter in consequence of this fall in temperature is

$$C_{\theta_1} \{(\theta'_0 + d') - (\theta''_0 + d'')\},$$

where C_{θ_1} is the capacity for heat of calorimeter and contents at the temperature θ_1.

If we neglect any small loss by radiation, &c., due to the differences d' and d'' between the temperature of the calorimeter and the surrounding walls, we may conclude that the whole of the heat thus evolved by the calorimeter was expended in the evaporation of water, hence

$$\Sigma q = C_{\theta_1} \{(\theta'_0 - \theta''_0) + (d' - d'')\}^* \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

Hence

$$\mathrm{ML} = \frac{e^2 n^2 \times t_e}{\mathrm{R}_1 \mathrm{J}} + \mathrm{Q}_s \times t_s + C_{\theta_1} \{(\theta'_0 - \theta''_0) + (d' - d'')\} \quad . \quad . \quad . \quad (4.)$$

In order to convey an idea of the relative importance of the terms in equation (4) I will here give the approximate *mean value* of each term resulting from the experiments described in succeeding pages.

TABLE II.

	$Q_e t_e$.	$Q_s \times t_s$.	Σq.
When $\theta_1 = 40$ and $n = 4$	2150	19·2	± 1·6
$\theta_1 = 30$ and $n = 4$	2305	32·9	± 1·2
$\theta_1 = 30$ and $n = 3$	1752	32·9	± 1·2

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* This apparently clumsy method of representing the quantity of heat evolved or taken up by the calorimeter was adopted because, as the method of experiment involved separate determinations of θ'_0, θ''_0, d' and d'', the actual temperature of the calorimeter at any time could only be obtained in this manner.

Although, of course, I had, when commencing these experiments, no exact knowledge as to the comparative values of the terms, some preliminary observations enabled me to form a rough estimation of their magnitudes and consequently of the degree of attention which should be devoted to their accurate measurement.

Section IV.—The Method of Maintaining the Space surrounding the Calorimeter at a Constant Temperature.

I have, in Paper J., given an account of the apparatus employed for this purpose, and full details and plates will be found on pp. 374–378 (*ibid.*).

In order, however, to give a general idea of the arrangements, and to save the reader the trouble of reference, I will here quote the brief description given in the abstract of that paper:—"The calorimeter was suspended within an air-tight steel chamber. The walls and floor of this chamber were double, and the space between them filled with mercury. The whole structure was placed in a tank containing about 20 gallons of water, and was supported in such a manner that there were about three inches of water both above and beneath it. The mercury was connected by a tube with a gas regulator of a novel form, which controlled the supply of gas to a large number of jets. Above these jets was placed a flat silver tube, through which tap-water was continually flowing into the tank, all parts of which were maintained at an equal temperature by the rapid rotation of a large screw. Thus, the calorimeter may be regarded as suspended within a chamber placed in the bulb of a large thermometer —the mercury in that bulb weighing 70 lbs. A change of 1° C. in the temperature of the tank-water caused the mercury in the tubes of the regulating apparatus to rise about 300 millims. Special arrangements were made by which it was possible to set the apparatus so that the walls surrounding the calorimeter could be maintained for any length of time at any required temperature, from that of the tap-water (in summer about 13° C., in winter 3° C.) up to 40° C. or 50° C."

I think the above summary, together with the section on Plate 4, will convey a sufficient idea of the apparatus.

Since 1892, I have made certain improvements, which I will briefly describe.

During my J. experiments the range of temperature was from about 14° C. to 26° C. In subsequent experiments when I have required to use the apparatus at higher temperatures, it was found that the oscillations in temperature became serious, in some cases amounting to $\frac{1}{50}$° C. This was due to the temperature lag of the large mass of mercury, so that when the gas was lowered by the action of the regulator the resulting in-flow of cold water lowered the tank temperature before the mercury had contracted sufficiently to again heat the in-flow. In Paper A. I have described as follows the arrangements made to meet this difficulty:—"As now arranged, when working above temperatures about 20° C., a small motor acts as a heart, and, the tap-water being shut off, pumps the tank-water itself round through the silver tube placed above the gas-jets. The water, by passing through the pump, &c., is slightly cooled; thus, the work of the regulator is confined to simply supplying the heat lost by convection, radiation, &c., and it performs this task admirably. As an illustration, I may mention that, in the series of over 50 experiments treated of in this communication, on only one occasion did the temperature of the steel chamber change by as much as $\frac{1}{100}$° C. throughout the duration of an experiment. On the solitary occasion that a change amounting to nearly $\frac{1}{50}$° C. was observed, the cause was found in the caking of the lime through which the gas was passed on its way to the regulator, and, in consequence, the experiment was discarded before working out its results."

On account of the use of the differential thermometers (see Section V.) employed in the present investigation, it was essential that any changes in the temperature of the steel chamber should be measured with greater accuracy than was necessary in my previous work, for now such changes influenced the temperature measurements, whereas on former occasions they only affected the loss by radiation, etc. An open range mercury thermometer placed in mercury in the hole E (Plate 4) gave the temperature of the walls surrounding the calorimeter and changes in the mean stem temperature had to be guarded against for the reason above given. The small motor already referred to now served another purpose. A portion of the water raised by the pump, instead of returning to the tank through the silver tube passed into a coil of about 20 feet of " compo. " tubing inserted in the tank, was then forced up a glass tube surrounding the stem of the thermometer, and passing out at the top, returned to the tank. Thus the stem-temperature was kept constant throughout an experiment, the regularity of the flow being secured by an overflow system. True, the water near the top of the glass tube would be slightly cooler than the tank water when working at high temperatures, but this was of no consequence, as the chief use of the thermometer was to detect *differences during an experiment.* Two thermometers labelled A and II. were used. Although an accuracy of an order of $\frac{1}{10}$° C. would have been sufficient in actual elevation, I compared these thermometers every 0°·5 C. of their ranges with two different Tonnelot thermometers, standardised by the Bureau International des Poids et Mesures, and also with my own platinum standard. The results of the separate comparisons (expressed on the nitrogen scale) agreed within ·005° C.

The stems of both thermometers were graduated in millimetres. A (range 16° to 26° C.) having about 27 millims. per 1° C. and II. (range 28° to 53° C.) about 20 millims. per 1° C. A table was constructed for the whole range of temperature, giving the value in degrees C. of (*a*) each millimetre of these thermometers in terms of the air thermometer, and (*b*) in terms of the millimetres of the "mean bridge wire scale" used by me for the determination of differences of temperature.

These thermometers were observed through a microscope fitted with a micrometer scale so divided that it gave 10 divisions to the millimetre. There was no difficulty in estimating $\frac{1}{10}$ of the micrometer divisions, and thus readings could be taken to ·01 millim., that is to about ·0004° C. on A and to about ·0005° C. on No. II.

I do not, of course, claim that I could determine *actual* temperatures to this closeness, by these or any other mercury thermometers, but, owing to the precautions above described, I have no doubt but that *changes* in temperature of the order of 0°·001 C. (*i.e.*, about ·025 millim.) could be detected, especially as any movement was extremely slow—in no case as much as 0°·01 C. per hour. A constant vibration, due to the pumping of the water up the surrounding tube, tended to prevent "sticking."

A further improvement has been the addition of a gas pressure regulator. This apparatus was designed for me by Mr. HORACE DARWIN, and is the only satisfactory instrument of the kind I have seen. It is most perfect in its action, and I am now absolutely indifferent to changes of pressure in the mains.

With these additions, I think that the whole of this constant temperature portion of the apparatus may be considered as nearly perfect. Only those who have watched it actually at work can appreciate the certainty of its action; it can be set with precision to any temperature between that of the tap-water and 64° (the highest temperature at which I have actually tested it), and my only regret is that circumstances compel me to leave unused, for the greater portion of each year, apparatus by means of which so many difficulties could be overcome.

Section V.—DESCRIPTION OF THE CALORIMETER AND ITS CONNECTIONS.

The calorimeter was made of brass and was of cylindrical form, 10 centims. in diameter and 10 centims. in height.

It contained a silver flask, F (see Plate 5, fig. 1), in which the evaporation took place; a stirrer, of which the lower end only is shown at S; a rack (shown in the horizontal section, Plate 5, fig. 2) which carried a coil of platinum-silver wire, and about 18 feet of silver tubing wound in a spiral—shown in section at *p.p'*. A platinum thermometer also passed from the top to the bottom. With so many objects crowded into so small a space, it is difficult to convey any clear idea of the internal arrangements, therefore I will only attempt a brief description, and shall rely chiefly on the sections given in Plate 5 to convey the necessary information. The capacity of the flask, F, up to the side opening at *d*, was about 68 cub. centims. Any vapour or gas passing from the flask into the spiral at *d*, after descending to the bottom of the calorimeter, ascended throughout the whole length of the coil, and thence up the tube *e*. This arrangement was adopted to diminish any chance of the carrying of the liquid, or "priming," by the flow of vapour or gas, as it appeared improbable that particles of liquid would be carried up a gentle slope of 18 feet in length.

Any inflow of gas came down the tube *f*, and passed directly into the bottom of the flask at *g*.

The stirrer S had two paddles, reaching from top to bottom of the flask; the blades and the central tube were of thin copper. Down this tube passed a steel shaft, which hung at the lower extremity within a hole in a sheet of brass projecting from the side of the calorimeter. The bearings of the stirrer were entirely outside the calorimeter, and the lower end did not touch the base, or bear on the surrounding plate, whose only purpose was to check vibration. The paddles had a slight "pitch," so as to throw the liquid upwards, as well as cause it to rotate. The exterior bearings at the top of the glass tube S (fig. 3) were of the kind figured in Plate 2, Paper J., and were certainly sufficiently air-tight to prevent any diffusion, even when the stirrer was rotating rapidly, but, as the calorimeter was filled with a non-volatile liquid, the air-tightness of this joint was of little consequence, especially as the temperature of the calorimeter remained constant during the experiments and the air-space above the liquid was small. The rubbing surfaces were very true and always immersed in oil, thus the heat generated must in any case have been unimportant. The greater portion of any heat developed in the external bearings would pass to the brass tube, of which they formed a part, and, as the lower portion of this tube was washed by the tank water, its temperature would in any case rise but little. Any heat passing down the steel shaft (length 28 centims., diameter 0·35 centim.) would, of course, be included in the "stirring correction," but I should imagine that it was in reality negligible, for about 4 inches of the glass tube down which it passed were also washed by the tank water.

Further, slightly above the top of the calorimeter a section of ivory was inserted in the stirring shaft, in order to diminish conduction as much as possible.

The platinum-silver coil was wound on small ebonite tubes surrounding the narrow brass pillars of the rack, whose section is shown at R (fig. 2). The method by which the insulation of the rack was maintained, where the two brass pillars R_1 R_2 passed through the top of the calorimeter, is shown by the section (Plate 5, fig. 4). It must be remembered that these junctions had not only to be perfectly insulated, but that they had also to be absolutely air-tight, over a considerable range of temperature (10° to 60° C.),* even to pressures of 1 atmosphere.

The platinum-silver coil was about 100 centims. in length, and so wound that it was completely immersed when the depth of the liquid was 4 centims. Two copper wires (B.W.G., 21) were soldered to each of the pillars R_1 and R_2 where they projected above the roof of the calorimeter at *l* and *l'* (fig. 3), thus, in the steel lid, there were four junctions similar to those above described (see Plate 6, fig. 3). The blocks of ebonite forming the top slab of the junctions were, however, in this case, made nearly five inches in length; they projected as far as the lid of the tank, and

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* The insulation of the whole circuit after all the apparatus was placed in position, was better than I could measure, *i.e.*, 10^7 ohms.

thus all contact between the leads and tank-water was prevented. The calorimeter was hung below the steel lid by five glass tubes, thus ten air-tight junctions of glass to metal were required, in fact, four of these junctions were, in reality, double ones, for the lower extremities of the narrow tubes *e* and *f* (Plate 5, fig. 1) had not only to be fixed into the lid of the calorimeter, but also joined on to the ends of the silver tubing. In like manner, where they passed through the steel lid, they had to join also on to glass tubes leading to two glass taps immersed in the outer tank. There were, therefore, practically fourteen such joints. I have previously described an alloy by which I was enabled to make these joints absolutely air-tight.* In order to show how carefully all these joints were tested, as well as several others in the external connections by which communication with the mercury pumps was established, I extract the following from Paper A. :—"In the spring of this year the intra-mural space was exhausted until the reading of the McLeod gauge connected therewith was reduced to 11, indicating a pressure of about 0·12 millim. The apparatus was then left untouched for a month, except that the temperature was occasionally raised or lowered, and at the end of that time the reading of the gauge was still less than 12. Dry air was then re-admitted to this space, and the silver flask, with its connecting tubes (embracing about 50 feet of tubing with several joins), tested in a similar manner. Those who have had to deal with low pressures will understand that, when all was found satisfactory, a great difficulty had been surmounted. I did not retain this vacuum during the experiments, as I felt that it would subject the glass tubes, &c., to a continuous strain which the conditions of the experiments rendered unnecessary. The labour had not been lost, however, for I was able to count with confidence on the gas-tightness of the whole apparatus."

Where the supporting glass tubes entered the calorimeter lid (as shown by the plan, Plate 5, fig. 3), they were surrounded by metal tubes (shown by the outer ring in each case) nearly 1 centim. in length which had their lower extremities soldered to the lid. The annular space between these and the glass tubes was filled with the alloy and the joints on the top of the steel lid, from which the apparatus hung, were of the same kind but slightly deeper. The tube S surrounded the stirrer shaft. The platinum thermometer AB passed down T, and this tube was also used for inserting or withdrawing the calorimeter liquid. The thermometer was wrapped with india-rubber tape so that the annular space between it and the glass tube T was made air-tight throughout the upper 4 inches.

Through *h′ h* communication was established between the exterior and the silver flask. During my earlier experiments a thermometer stood in this tube with its bulb nearly at the bottom of the flask. It was of course possible to render air-tight the connection between the thermometer stem and the top of the tube *h′*, where the latter projected above the tank. This would not, however, have been sufficient, for the flask contained a volatile liquid, and distillation would

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* 'Cambridge Phil. Soc. Proc.,' 1893.

have taken place into and out of the annular space between the tube and thermometer stem, according as the calorimeter was warmer or cooler than the tank water. This thermometer had also to be frequently removed in order to insert liquids into the flask, and therefore any junction at the bottom could not be made a permanent one. The difficulty was surmounted as follows:—The silver tube *k* (Plate 5, fig. 1), which passed up from the lid of the silver flask was soldered to the calorimeter lid, above which it projected. A hollow brass rod just fitting the glass tube, but with its lower end tapered, was, before fixing the glass in place, held vertically with the tapering end filling the open end of the silver tube. The annular space between the silver and surrounding brass tube was then filled with the melted alloy, to above the top of the silver, and the glass tube lowered into its final position. When the alloy hardened, the brass rod was loosened by lowering into it a red-hot wire. The lower inch or so of the brass rod having been cut off was then placed co-axially round the thermometer stem and made one with it by filling the annular space between it and the stem with the same invaluable alloy. Thus, on lowering the thermometer into its place, the brass tube almost exactly fitted into the ring of alloy at the bottom of the glass tube. The fit was made good by prolonged grinding with rotten stone—using the thermometer stem as a rotating shaft. The result was a practically air-tight join at the calorimeter lid. It must be remembered that as the air-tightness was secured by the cork at the upper end, this joint had not to stand any pressure, but was only required to prevent diffusion.

I have, for two reasons, fully described this method of fixing the tube. (1) I thereby overcame a difficulty which had perplexed me for a long time; (2) it was necessary to explain the constriction at the lower end of the tube *h*, which in its turn became a source of difficulty when I altered my method of experiment.

l and l_1 (fig. 3) are the insulating junctions for the rack on which the coil was wound.

The base of the calorimeter, which was not fixed until everything else was in place, was heated until solder contained in the circular trough, of which a section is shown at M (fig. 1), became fluid; the calorimeter was then pressed down upon it, and, as soon as the solder commenced to harden, the calorimeter was set in cold water. The base was thus soldered on without melting the alloy in the lid or injuring the internal fittings.

The whole apparatus was a difficult and complicated one to construct, and I owe my sincere thanks to Mr. THOMAS for the ingenuity and patience he devoted to the task. My brief description can convey but little idea of the many difficulties that had to be surmounted between the conception and completion of this apparatus, and I may mention that although commenced in February, 1893, it was not until the spring of this year (1894) that the calorimeter could be regarded as completed.

Exterior Connections.

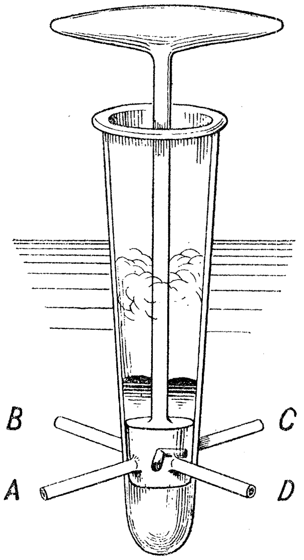
The upper end of the narrow glass entrance tube *f* (Plate 5, fig. 1) was, as before stated, connected with a glass single-way tap, T_3 (Plate 6, fig. 1), which, on the further side was connected with about 30 feet of thin-walled copper tubing immersed in the tank water. Thus, all gas entering the silver flask through T_3 would be at the temperature of the tank water, and (the calorimeter temperature being identical with that of the tank) no heat would be added or subtracted when gas was passed through the flask and spiral. T_4 was a four-way tap on the exit side, the arms of the one passage through its core being at right angles to each other. The tap is shown in fig. 1 (*infra*). A is the tube leading from the flask and connected with *e* (Plate 5, fig. 1). By rotating the core, A could be connected with B or D, or C could be connected with B or D. The glass tubes forming the outer case of both taps T_3 and T_4 were sealed at the lower extremity, and after a portion of the tube above the core had been filled with mercury, these taps were perfectly air-tight. The outer glass tube of each was about 6 inches long, thus the lower 4 inches were below the surface of the tank water, and the upper parts of the tubes were packed with cotton wool. The cores narrowed to a glass rod, which, passing through the wool, projected above the tank lid, where a handle was attached ; thus the taps could be opened or shut from the exterior of the whole apparatus. The position of the taps is indicated in Plate 6, fig. 1.

Tube B (fig. *infra*) which communicated with the apparatus into which, during my earlier experiments, the vapour was passed, extended under the surface of the water to the walls of the tank, it then passed above a row of small gas jets, and thus no condensation took place until the vapour arrived at the drying bulbs. At the close of an experiment a movement of the tap connected C and B, and as C was connected by a three-way tap (T_2, Plate 6, fig. 1) with the dry air supply, any moist air remaining in B or its continuation was swept into the receiving apparatus. On the other hand, by connecting A and D before the commencement of an experiment the vapour brought by the gas which had passed through the calorimeter was disposed of without affecting the weight of the receiving apparatus attached to B. Thus an experiment could be started at any moment by changing the connection at tap T_4 from AD to AB, and that without altering in any way the conditions as to flow of gas, rate of evaporation, &c.

Finally, I would remark that throughout the gas circuit, the gas only came into contact with the following materials—glass, silver (only hard solder was used for all the flask and tube connections), the glass-metal-joining alloy at the junctions, and the drying agents. True, in my "exhaust" experiments with water the vapour had to pass through about half-an-inch of thick rubber on the exit side, where connection was made with the condenser, but when using other liquids, this joint can easily be replaced by a glass one. When evaporating ether (with which I have made some preliminary experiments), the grease on the cores of the glass taps was replaced by a trace of phosphoric acid, which appeared to answer admirably. Thus, the apparatus can be used without alteration for all volatile liquids which do not act on the metals, a possibility I kept steadily in view when designing it.

Fig. 1.

Four way tap T_4



[May 4, 1895.—At the meeting of the Physical Society on January 11, 1895, Professor Ramsay exhibited an apparatus by means of which the comparative latent heats of evaporation of different liquids could be determined. I had the pleasure of seeing the apparatus at work, and from that time I abandoned all idea of extending my own investigation to other liquids than water. The method adopted by Professor Ramsay is so perfect, and at the same time so simple, that I feel that it would be waste of time and energy to pursue my absolute determinations. I mention this because many of the precautions described in the preceding sections were adopted with the view of conducting experiments with various liquids, and (as I now discover) might have been dispensed with.

Professor Ramsay now informs me that, although certain practical difficulties in the working of his apparatus have not as yet been entirely overcome, he has already determined (approximately) the comparative latent heats of evaporation of a considerable number of volatile compounds, and that the results will shortly be published.

I venture, however, to call attention to the fact that the very perfection of Professor Ramsay's method increases the importance of an accurate knowledge of the absolute latent heat of evaporation of water.]

Section VI.—THE DETERMINATION OF Σq.

I will now describe the method of obtaining the value of the various terms in Equation I. (p. 272) by which the quantity of heat supplied during an experiment is ascertained.

Σq is the quantity whose accurate determination presented the greatest difficulty, therefore the apparatus was so designed as to reduce this term to as small dimensions as possible, and since many of the contrivances adapted to this end may, unless their purpose is explained, appear unnecessary and cumbersome, I commence with this term in order to avoid repetitions.

Had it been possible to so arrange matters that the temperature of the calorimeter at the beginning and end of an experiment should be absolutely unaltered, this term (Σq) would have vanished, and in my earlier experiments, during which I endeavoured to determine the mass of water evaporated by passing the resulting vapour through drying bulbs, this condition was practically fulfilled, since it was always possible to stop an experiment at any time. I was compelled, for reasons which will be given later, to abandon this method of estimating M, and to adopt a method in which a given mass of water was to be evaporated. The observer had, therefore, no choice as to the time when the experiment should be completed, and as the thermal balance could not be absolutely maintained throughout an experiment, it was impossible to ensure the identity of the initial and final temperatures.

It was advisable, if possible, to so arrange matters (I.) that a small alteration in the quantity of heat should produce a considerable change in temperature, so that small differences in the thermal equilibrium might render themselves evident; (II.) that the oscillation in temperature might be reduced to as small dimensions as possible; (III.) that the difference, if any, between the initial and the final temperatures should be accurately measured.

Although Nos. I. and II. appear contradictory, such is not the case, for the important matter was to ensure the equality of the thermal, as distinct from the temperature balance; therefore, if small alterations in the former made themselves readily evident by changes in the latter, and if the latter changes were kept small, the desired end was attained.

Within the calorimeter there were two agencies at work—the cooling due to the evaporation (which for convenience I shall henceforth venture to speak of as a "supply of cold"), and a supply of heat due to the current; therefore, unless some means were adopted of rapidly bringing the contents to a uniform temperature, the temperature gradient from the hotter to the colder portions would be considerable. It was thus necessary to completely fill the calorimeter with some liquid and to rapidly stir this liquid.

Two objections to the use of water immediately presented themselves: (*a*) its great capacity for heat (which would have caused changes in the thermal balance to have but a small effect on the temperature); (*b*) its electric conductivity, which would have necessitated the covering of the platinum-silver coil with some insulator.

I therefore gave my first attention to the selection of some more suitable liquid. The ideal one ought to have small "volume heat,"* and should be a perfect insulator, and therefore I at first selected aniline. I determined its specific heat over a range of from 15° to 52° C., and found that in some respects it suited my purposes admirably. A full description of this work will be found in paper A.

Early in September I had, in consequence of an accident, to take the calorimeter to pieces and withdraw the aniline. I was then alarmed by the darkening in colour which it had undergone. In the discussion on the paper above referred to, Dr. ARMSTRONG expressed his opinion that the change in constitution indicated by this change in colour was not of a nature to render it likely that it would produce any appreciable effect on the specific heat, as it was probably due to the formation of a body whose properties were similar to those of aniline. I may add that Professor RAMSAY independently expressed an opinion to the same effect. My observations show that no alteration in the specific heat of aniline had been indicated by the change in colour referred to, and I am still of opinion that it may be regarded as a liquid admirably adapted for calorimetric purposes, as it is but rarely that it would be required for experiments extending over a period of months or years.

If I am able to carry out my investigations into the latent heat of evaporation of water and other liquids according to the plan I have designed, it is probable that the enquiry will occupy my leisure time for some years, and as the exact determination of the capacity for heat of the calorimeter and contents throughout a large range of temperature is a most laborious one, I was anxious to employ some liquid about the constancy of whose composition I should have no anxiety.

At this time, Mr. THOMAS suggested to me that I should try a particular kind of petroleum oil supposed to consist of hydrocarbons only. This is a singularly limpid oil, without colour, smell, or taste. I tested its insulating powers very severely over a range of temperature 10° to 150° C., and although I placed two large electrodes within a quarter of an inch of each other, and used a potential difference of 10 volts, I could cause no permanent deflection in a high resistance galvanometer throughout this range of temperature. Its specific gravity at 15° is ·865, and, as I shall show hereafter, its "volume heat" is smaller than that of aniline.† After several experiments of different kinds, I came to the conclusion that this oil was a most suitable liquid for my purpose.‡

The replacement of aniline by oil necessitated a re-determination of the capacity

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* I propose to use the above term to denote the capacity for heat of any volume of a substance as compared with the capacity for heat of an equal *volume* of water. The phrase has already been used in a similar sense by DEELEY, 'Chem. Soc. Journ.,' 1893, p. 854.

† This oil appears to me to be well adapted to many physical purposes.

‡ See note at end of this Section.

for heat of the calorimeter and its contents throughout my range of temperature, and as far as regards the purposes of the present enquiry, a great portion of my work on aniline was rendered useless. The method employed during the aniline investigation necessitated a repetition of the experiments with different masses of aniline and with different electromotive forces. As, however, those experiments had given me a very exact determination of the capacity for heat of the calorimeter itself throughout the range of temperature 15° to 52° C., the whole of the labour had not to be gone through again, for (the "water equivalent" of the calorimeter being known) it was not necessary, when using oil, to repeat the experiments with different masses.

In Appendix II., I give particulars of the method employed for determining the capacity for heat of the calorimeter and contents at different temperatures.

The following table gives the results, and as the value of the specific heat of this oil at different temperatures may be of use to other experimenters, I have also given (in terms of a thermal unit at 15° C.) the capacity for heat (C_{θ_1}) of calorimeter and contents at temperature θ_1 (N scale), and the specific heat of the oil S_1. The mass of oil (corrected to *vacuo*) = 474·02 grams.

TABLE III.

θ_1.	C_{θ_1}.	S_1.	$\cdot 4830 + (\theta_1 - 20) \times \cdot 00087$.
20°	307·50	·4830	·4830
30	312·38	·4917	·4917
40	317·79	·5006	·5004
50	323·14	·5092	·5091

The tables in Appendix II. show that the numbers in Column III. are *direct experimental results,* not "smoothed" in any way.

It is noticeable that the value of S_1 is a linear function of θ_1 throughout the above range, although the curvature of the line giving the capacity for heat of the calorimeter is very marked.

Probably these results are correct to better than 1 in 1000 (see Appendix II.), but, as an inspection of Table II. will show, an order of accuracy of 1 in 10 would have been sufficient. As, however, the accurate determination of C_{θ_1} and S_1 involved (by the method adopted) little more labour than an approximate determination, I thought it advisable to ascertain the specific heat of the oil with accuracy.

Since $\Sigma q = C_{\theta_1} \{(\theta'_0 - \theta''_0) + (d' - d'')\}$ and C_{θ_1} varied from 307 to 323, it is obvious that if Σq was to be kept small, the changes in θ_0 and d must be very limited, and that such changes must be measured with extreme care. Having already described the manner in which the temperature of the surrounding walls was kept constant, and the way in which any small variations in θ_0 were ascertained, I now indicate the method of measuring the values of d' and d'' (*i.e.*, the initial and final differences between the temperature of the calorimeter, θ_1, and that of the surrounding walls, θ_0).

As differences of temperature had now to be dealt with, the use of differential thermometers naturally suggested itself.

The following extract is taken from a full description of these thermometers given in my Paper A. (see also Plate 6, fig. 2):—

"Two platinum thermometers (labelled AB and CD) were constructed with great care; four stout platinum leads passed down the stem of each, supported and insulated in the usual manner by small disks of mica, and the resistance of all these leads was made as equal as possible before attaching the coils. Great attention was given to this matter, and it is probable that the leads in no case differed amongst themselves by 1 in 10,000. The coils, consisting of a particularly pure sample of platinum wire, were then attached, and several days were devoted to securing their equality Their resistance in ice was about 18 ohms, thus $\frac{1}{1800}$ of their resistance could be directly determined on the box. The galvanometer swing was about 500 for a change of ·01 in the box; and such equality was secured that when both thermometers were placed in ice (the necessary precautions being taken with regard to exterior connections, &c.) no readable difference in the swing of the galvanometer could be observed; thus they differed by a quantity certainly less than 1 in 100,000. This equality, although not a necessity, was a great convenience.

"Although cut from the same length of wire, and insulated in a precisely similar manner, the coils did not possess exactly the same coefficients. The resistances in steam and sulphur were repeatedly determined and checked by observations in the vapour of aniline. Both thermometers were on several occasions heated to a red heat, the hard glass tubes containing them becoming slightly bent in the process; but, since this annealing, no further change has been observable in them. The method of completely standardising such instruments has been fully described by Professor CALLENDAR and myself in 'Phil. Trans.,' 1891, A, and I need not, therefore, here dwell upon it. The values of δ differed slightly, viz., 1·513 and 1·511; but such a difference, even if not allowed for, would, over the range 0° C. to 100° C., in no case cause an error exceeding about $\frac{1}{2000}$° C. in elevation. These thermometers were so connected that the compensating leads of AB were placed in series with the coil of CD, and *vice versâ*. Any heating of the stem of AB or CD, therefore, added an equal resistance to each arm of the bridge; and, as the leads were everywhere bound together, the indications were absolutely independent of all changes in temperature except those of the bulbs.

"The two thermometers, with their leads connected as described, were placed at opposite ends of a bridge-wire of platinum-silver. During the spring of this year this wire was subjected to a most careful calibration by what was practically CAREY FOSTER's method, and it proved to be more unequal than I had expected. It was therefore re-calibrated by a different method in which a resistance-box was used as a shunt, and the agreement between the results was satisfactory. The whole wire was 80 centims. long and had a total resistance of about 0·4 ohm. For convenience, and to avoid thermal effects, a similar wire connected with the galvanometer was laid alongside it, and the sliding-piece was fitted with a screw so arranged that a small turn of the screw-head made contact with both wires.

"The wire and contact maker were covered by a thick copper shield (the screw-head projecting through a narrow slot) passing from end to end of the bridge. Thus the temperature of the wire was kept uniform. By means of a vernier, the divisions on the scale could be read to $\frac{1}{10}$ millim., which with this wire and thermometers AB and CD indicated at 50° C. a temperature difference of ·000915° C. The temperature coefficient of this wire was found to be ·00029. The resistances of the different parts of the wire were, after correction for the errors of individual coils, &c., merely expressed in terms of the mean box ohm, the absolute value being of no consequence so long as the fixed points were determined in terms of the same standard. The remaining two arms of the bridge were constructed of german-silver. They were wound together, boiled in paraffin, placed in a bottle, and I expended much care in finally adjusting them until equal. Their resistance was about 5 ohms, and that of the galvanometer about 8 ohms, which, assuming the resistance of the thermometers as about 20 ohms each, would give nearly the maximum of sensitiveness. A single storage-cell was always used, and a resistance of 40 ohms was placed in the battery circuit when the thermometers were in ice. A table was then calculated which gave the resistance necessary in the battery circuit when the thermometers were at any temperature in order that C^2R (where R is the thermometer resistance) should be constant. Thus the rise in the temperature of the thermometer-coils due to current-heating was always the same, and consequent errors were eliminated, a point to which I attach considerable importance.

"The value of $R_1 - R_0$ in thermometer AB was 6·88815; therefore a difference of 1 ohm at 50° C. indicated a difference of 14°·5177 C., and as

$$\frac{dpt}{dt} = \left\{1 - \delta\,\frac{2t - 100}{100^2}\right\},$$

the degree value of any bridge-reading at other temperatures can be deduced.

"There was no difficulty, in the arrangement above described, of reading with certainty a difference of $\frac{1}{1000}$° C., and, as an illustration, I may mention the fact that if the thermometers were placed in separate hypsometers side by side on the bench and one of the hypsometers was then removed to the ground (about 3 feet below), the difference in the bridge-wire reading thus caused slightly exceeded ·4 millim."

In the paper above referred to, further particulars are given regarding the standardisation of these thermometers. During the experiments there described they were used to determine the rate of rise in the temperature of the calorimeter, whereas, in the work I am now describing, they were used chiefly as detectors of any difference of temperature between the calorimeter and the surrounding walls, and I therefore omit the details of the determination of their fixed points, &c., although I must add some other facts which are of importance for the present purpose.

The bridge-wire scale was so fixed that the mark 60 centims.* fell exactly in the middle. Had the bridge-wire been uniform therefore, and had the coefficients of the two thermometers been always the same, then when both were at the same temperature the bridge-wire reading would necessarily have been always 60 centims. I have stated that the thermometer resistances might be regarded as practically equal when both were in ice. The bridge-wire reading, however, was found to be 598·35 millims., when AB and CD were both in ice. At first sight this appeared to indicate a difference in the resistances of the two thermometers at 0°, but when the calibration of the bridge was concluded, it gave 598·4 millims. as the middle point of the bridge and thus afforded independent proof of the truth of the calibration and of the equality of the coils forming the other two arms of the bridge. Owing to the slight difference above referred to in the coefficients of the two thermometers the reading of the bridge null-point was found to be 601·4 millims. when both thermometers were at 100°. Now (as described in Paper A.) the fixed points of these thermometers in ice, steam, aniline, and sulphur-vapour, had been repeatedly determined with extreme care. I have, since the conclusion of these experiments (*i.e.*, on November 4), again taken the values of R_0 and R_1—ice and steam. They remain practically unchanged and are as follows :—

	AB.	CD.
R_1 . . .	24·58526	24·58333†
R_0 . . .	17·69711	17·69720
$R_1 - R_0 =$	6·88815	6·88613

Thus the difference between AB and CD would, when in steam, exceed their difference in ice by ·00198 ohm. Now the value of 1 millim. of the bridge-wire at reading 60 was 1·0020 times the mean bridge-wire millim., and the value of the mean bridge millim. was ·00062875 box ohm. Thus 1 millim. of bridge-wire at 60 = ·0006300 box ohm. Hence the movement of the two thermometers from ice to steam ought, according to the standardisation, to have caused a movement of $\frac{198}{63}$ millims. = 3·1 millims. On placing both thermometers in steam at 100° the actual bridge-wire reading was found to have altered from 598·35 to 601·40, a

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* The scale was marked from 20 to 100 centims.

† Expressed after correction for individual coil errors, &c., in terms of my "mean-box" ohm (Paper J., p. 409). The absolute values being of no consequence, I have, in order to save arithmetic, expressed the resistances of all my platinum thermometers in "mean-box" ohms.

change of 3·05 millims.; thus, entirely independent methods agree in giving the following formula as a sufficiently close approximation for the bridge-wire null-point at any temperature θ, viz.,

$$\text{N.P.} = 598{\cdot}35 + {\cdot}03\theta.$$

True, the coefficient of θ should be slightly larger, but I did not profess to read the vernier to nearer than ·05 millim. during the calibration of the wire, and therefore any closer approximation would be useless.

As even a small difference between the average temperature of the calorimeter and the surrounding walls would have some effect in experiments lasting more than an hour, the agreement between the results obtained by the different methods above described was extremely satisfactory. In addition I carried out a series of observations with both thermometers strapped together and immersed in the rapidly-stirred tank water, the temperature of which was gradually raised from 15° to 54°, and the position of the bridge-wire null-point was found throughout that range to be accurately given by the above formula.

The galvanometer was observed by means of a microscope fitted with a micrometer eye-piece by ZEISS. The swing was very "dead beat" and very uniform for a given D.P. The $\frac{1}{10}$th of a division could be estimated without difficulty by anyone accustomed to the instrument, and it was found more convenient to read and enter swings with $\frac{1}{10}$th of a division as unity rather than to express the fractions as decimals. Thus a swing of 2·5 divisions was entered as 25. I mention this as otherwise the swings given in the tables might appear curiously large. Occasionally the swing due to a change of 1 millim. in the bridge-wire reading was observed, but as the E.M.F. used was constant, and the galvanometer control-magnet was not re-adjusted during these experiments, the swing for a given change was found to remain practically constant when the temperature of the thermometers was unchanged. As the resistance of two arms of the bridge altered when θ altered, the swing varied slightly when θ changed, but the arrangement, above described, for keeping C^2R constant, diminished the extent of this change. A swing of 90 corresponded to a change of 2 millims. in the bridge-wire reading when $\theta = 40°$, and the swing at 30° was about 94.

The swing was of course obtained by reversing the battery connections and was thus independent of thermal effects, changes in the position of the galvanometer zero-point, &c.

Now, as above stated, a change of 1 millim. of bridge-wire about the reading 60 centims. indicated a difference of ·0006300 box ohm. If therefore the bridge-wire reading was at the null-point a swing of 10 indicated a difference of $\frac{2}{9}$ of ·0006300 = ·000140 ohm in the resistance of the two thermometers.

The following Table (calculated from the constants of the thermometers by means of the formula on p. 286) gives the change in temperature (on the N scale) corresponding to a change of 0·1 box ohm in thermometer AB*.

TABLE IV.

Temp.	ΔR (box ohms).	Δ *pt*.	Δθ.
°		°	°
20	0·1	1·4518	1·4387
30	0·1	1·4518	1·4430
40	0·1	1·4518	1·4474
50	0·1	1·4518	1·4518

Now the value of the *mean* millimetre of the bridge-wire (at temperature 15°) was ·00062875 box ohm, hence the following Table which (col. 2) gives the difference in θ indicated by a difference of 1 mean bridge-wire millim. from the bridge-wire null-point at the given temperature, and (col. 3) the difference in temperature indicated by a swing of 10 when the contact-maker is on the null-point.

TABLE V.

Temp.	Δθ for difference of 1 mean millim. b.w.	Δθ for swing of 10.
°	°	°
20	0·009046	0·001865
30	0·009073	0·001930
40	0·009101	0·002022
50	0·009128	0·002074

Before an experiment, the contact-maker was set, with the aid of a magnifying glass, to the exact null-point corresponding to the temperature at which the experiment was to be conducted, and it was left untouched throughout the experiment.†

The initial and the final swing rarely exceeded 30 or 40, and could certainly be read with a limit of error of 2, when only one observation was taken, and as, at these times, three observations were meaned (they were, by the way, usually identical), the

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* As AB was the thermometer immersed in the calorimeter it is with changes in its temperature that we have chiefly to do.

† An error of ·05 millim. in the setting of the bridge-wire contact-maker would correspond to a difference of ·000455° at 40°, and the radiation, &c., due to such a difference would be negligible. The radiation, &c., coefficient of this calorimeter when full was about ·00009 per 1° per sec., or the loss in temperature due to a difference of 1° would be about ·324° = 100·4 thermal grams per hour (assuming the capacity as 310), thus a difference of ·01° throughout an experiment would have caused a loss or gain of 1 thermal gram. Of course, the differences in temperature rarely attained to ·01°, and again, the differences were alternately + and −, so that the radiation, &c., loss or gain was evidently negligible. The radiation, &c., coefficient can be deduced from the experiments on the rate of rise made when determining the value of C_{θ_1} (Appendix II.).

probable error was certainly less than 2, and, I believe, less than 1). Assume the probable error to be as great as 2, it follows that the differences of temperature could be determined to ·0004°, and I am confident that differences of ·0001° could be detected.

There can be little doubt therefore that the quantity $\Sigma q = C_{\theta_1} \{(\theta'_0 - \theta''_0) + (d' - d'')\}$ could be determined to a far higher degree of accuracy than subsequent experience proved to be necessary.

NOTE.—December 4, 1894. At Mr. HEYCOCK'S suggestion, I have to-day tested as follows the oil supplied to me by Mr. THOMAS, and referred to in the preceding section. We placed a lump of sodium in a test-tube filled with the oil, and gradually raised the temperature to above 160° C. No action whatever was visible, and the surface of the melted sodium remained as bright as that of pure mercury. We may assume, therefore, that the manufacturers are justified in their statement that it consists of hydrocarbons only, and the probability that different samples would possess approximately the same composition is sufficient to make the determination of its specific heat of some value.

Section VII.—THE HEAT DUE TO THE STIRRING (Q_s).

I have already pointed out the necessity for rapid stirring. Throughout these experiments the stirrer revolved at a rate of about 310 to 320 revolutions per minute, which is a slow rate as compared with that adopted during my enquiry into the value of J. The conditions, however, are different. In my former work I had at times to make observations with the calorimeter only partially filled with liquid, and I found that unless the water was thrown over every part of the calorimeter, its capacity for heat varied with the depth of the liquid. Throughout my present work the calorimeter was full, the liquid almost touching the lid, and, in consequence, I considered the slower rate sufficient to ensure an even distribution of temperature.

In my aniline experiments previously referred to, I eliminated the effect of the stirring-heat by finding the temperature (θ_N) at which the stirring supply exactly balanced the loss by radiation, &c., and thus the rate of rise at θ_N enabled me to determine the effect of the electrical supply. As throughout my observations on latent heat I had to maintain the temperature of the calorimeter at an equality with the surrounding walls, this mode of elimination was not applicable.

Two methods of finding the value of the mechanical supply suggested themselves.

I. That of finding the mass of water which it was necessary to evaporate per hour in order to maintain the calorimeter at a constant temperature, when the supply of heat was that due to the stirring only.

II. That of determining the rate of rise across the null-point (*a*) when the heat supply was that due to stirring only; (*b*) when the heat was due to the stirring and a given potential difference.

I. I made a large number of determinations by this method, especially during the "preliminary experiments," of which an account is given in Section IX., where the evaporation was promoted by passing a current of dry gas through water.

As I shall give details of the operations when describing the "preliminary experiments," I will not enter into particulars here, but I may now mention that the results by this method were by no means satisfactory, either as regards the determination of the stirring heat supply (Q_s) or of the values of L. The discrepancies in the value of Q_s are, however, not alone sufficient to explain the comparative failure of this method of finding L, for when both the rate and the temperature were the same, the variations in Q_s never attained to 1 in 20, and as Q_s was but about one-hundredth of the total supply, the approximation was nearly sufficient. I omit any detailed account of these experiments, as I made no use of them in my final calculations, and it would needlessly fill much space. I will, however, give the conclusions they led to, as they corroborate the results obtained by the method finally adopted.

Let

m_s = mass of water evaporated per 1 second by the stirring supply,

and

r = the rate of stirring (*i.e.*, number of revolutions per second).

When θ_1 diminished, the value of m_s increased, and this rate of increase was much greater after the aniline was replaced by oil; the change being evidently due to the increase of viscosity as the temperature diminished. When the stirring took place in aniline m_s varied very nearly as r^2, but when oil was the liquid m_s varied nearly as r^4.

In a former paper[*] I have proved that when the liquid was water the stirring heat varied almost exactly as r^3, and I gave particulars of 108 experiments bearing out that conclusion. Again, in Paper A., I have shown that when using aniline with a different form of stirrer $Q_s \propto r^2$ approximately. Now with the same stirrer as that used in aniline we get with oil $Q_s \propto r^4$; at 50° the power of r should be slightly higher, at lower temperatures rather smaller. These differences, although surprising, are none the less real.

In the case of water the conditions were so different (*e.g.*, r was about 30 instead of about 5) that no comparisons could be drawn, but, in the case of the aniline and the oil, the conditions were almost identical. My incredulity with respect to the relations between Q_s and r led to considerable delay, as I repeated these experiments unnecessarily, and it was not until a different method of observation led to the same conclusion that I felt any confidence in the results.

II. I now pass to the method indicated in II. (*supra*), in which no weighings were involved, and where I was also able to dispense with the passage of air through the apparatus.

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[*] Paper J.

Let t be the time of rising through a small range of temperature from below to above the surrounding temperature (θ_0).

If the heat supply is in one case due to both an electric current and the stirring, and in another to the stirring only, we have

$$(d\theta_1/dt)_{\epsilon s} - (d\theta_1/dt)_s = (d\theta_1/dt)_\epsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{I.}),$$

where θ_1 is the temperature of the calorimeter, and the suffix denotes the nature of the supply.

And (using the notation on pp. 272 and 273)

$$(d\theta_1/dt)_\epsilon = \text{Q}_\epsilon/\text{C}_{\theta_1}, \quad \text{and} \quad (d\theta_1/dt)_s = \text{Q}_s/\text{C}_{\theta_1},$$

therefore

$$\frac{\text{Q}_s}{\text{Q}_\epsilon} = \frac{(d\theta_1/dt)_s}{(d\theta_1/dt)_{\epsilon s} - (d\theta_1/dt)_s} = f \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{II.}).$$

Eq. (II.) will be true on any scale, and thus it is unnecessary to convert the bridge-wire readings into degrees C., and since

$$\text{Q}_s = f\text{Q}_\epsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{III.}),$$

if e, n, and R_1 be known, we can find Q_s, for

$$\text{Q}_\epsilon = e^2n^2/\text{R}_1\text{J} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{IV.}).$$

Thus Q_s can be found, although the capacity for heat of the calorimeter and contents and also the scale of temperature are unknown.

If we convert the bridge-wire degrees into C. degrees (N. thermometer) then, since

$$(d\theta_1/dt)_{\epsilon s} - (d\theta_1/dt)_s = \text{Q}_\epsilon/\text{C}_{\theta_1},$$

we get

$$\text{C}_{\theta_1} = \frac{\text{Q}_\epsilon}{(d\theta_1/dt)_{\epsilon s} - (d\theta_1/dt)_s} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{V.}),$$

and thus C_{θ_1} can be found.

In Appendix I. I give particulars of the experiments by which the values of Q_s for different values of θ_1 were found. I regret that the observations are so few in number. Unfortunately I did not adopt this mode of experiment until the eleventh hour, and as these experiments were very lengthy, I should consequently have been unable to complete sufficient direct determinations of L to establish its value at the two points to which want of time compelled me to limit the investigation.

On comparing the results with those obtained in oil by the previous method, I found that the agreement was sufficiently close to warrant a postponement of further investigation on this point, and I am confident that the values of Q_s given in the following table are correct to better than 1 in 50, at temperatures 30° and 40°, although I am less certain about the values at 20° and 50° C.* The latter, however, are not required for the purposes of this paper, except in so far as they affect the specific heats of the oil in Table III.

TABLE VI.—Thermal grams per sec. (Q_s) at rate (r) 5·300 revolutions per sec.

θ_1.	Q_s.	$\frac{Q_s}{r^4} = k$.
50°	·00235	298×10^{-8}
40	·00466	590×10^{-8}
30	·00665	843×10^{-8}
20	·00834	1056×10^{-8}

Let Q'_s be the thermal grams per second due to a rate r_1.

Then

$$Q'_s/r_1^4 = Q_s/r^4 = k,$$

therefore

$$Q'_s - Q_s = k\,(r_1^4 - r^4),$$

therefore

$$Q'_s = Q_s + k\,(r_1^4 - r^4) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1.)$$

Hence

Temperature 40°, then $Q'_s = \cdot00466 + (r_1^4 - 789) \times \cdot0000059$.

,, 30°, ,, $Q'_s = \cdot00665 + (r_1^4 - 789) \times \cdot0000084$.

I do not, of course, suppose that $Q_s = kr^4$ is the exact relation. I have already indicated that r^4 was too small at high, and too great at low temperatures. It must be remembered, however, that the variations in r were small, and thus the relation is sufficiently close for the correction of such variations as occurred during these experiments.

If we assume that the work done (for a given value of r) is proportional to the viscosity, the values of Q_s denote how great a change in viscosity is produced by raising the temperature from 20° to 50°. I repeat, however, that the values at 20° and 50° must be regarded with suspicion.

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* I have no corroborative experiment (by the former method) at 20°, and only one at 50° (see Appendix II.).

Section VIII.—MEASUREMENT OF THE HEAT DEVELOPED BY THE CURRENT (Q_e).

A sketch of the electrical connections is given in Plate 6, fig. 3, and a full description will be found in Paper J., pp. 382–388, therefore I will here give only a brief description.

Measurement of E.

Leads marked 2 and 4 were connected with the storage cell circuit, leads 1 and 3 with the Clark cells. A special form of rheochord was used consisting of two long barometer tubes (7 feet in length), which were so arranged that they could be raised or lowered by the rotation of handles; thus the length of the vacuous space could be altered at will. Platinum wires passed down these tubes into the mercury. The wires were placed in parallel arc and thus one acted as a shunt to the other. The change in resistance depended, therefore, not only on the movement but on the ratio of the two resistances, and the instrument could be set so that a large movement caused but little change, or *vice versâ.* The contact between platinum and mercury *in vacuo* was found to be very satisfactory. The resistance of the storage circuit could thus be altered at will. The Clark cell circuit contained a high resistance galvanometer G_1, with a resistance of about 9000 ohms, and joined the storage circuit *at the roof of the calorimeter* (at M and N, small sketch, Plate 6, fig. 3). By adjusting the rheochord the ratio of the external resistance of the storage circuit to the coil resistance could be altered at will, so that the D.P. at the ends of the coil became equal to that of the Clark cells, and the balance was maintained by watching the indications of G_1, and, when necessary, adjusting the rheochord. The spot of light from G_1 passed down a tunnel 4 feet in length on to a sheet of ground-glass placed opposite the rheochord. In Paper J., p. 384, I have given the experimental numbers on which the following statement was based:—

"It thus appears that the variations in E (the potential difference at the ends of the coil) were certainly within $\frac{1}{100000}$ of the mean value during the experiments, and changes in E, consequent on changes in the coil resistance, or the E.M.F. of the storages, could be disregarded."

The effect of any error in determining E would be serious (the quantity E^2 being used in the reductions), and hence its accurate measurement was of great importance. I am satisfied, however, that (assuming the value of E for the Cavendish standard Clark cell to have been accurately determined) no error in the measurement of Q_e is due to uncertainty as to the potential difference. The thirty-six Clark cells used have been fully described, in Paper J., pp. 385–388, as well as in the Paper by Messrs. GLAZEBROOK and SKINNER.* They have been compared with each other at regular intervals up to the present time, and their relative changes are small. At least three of these cells were always placed in parallel arc. Sometimes when

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* 'Phil. Trans.,' A, 1892, pp. 622–624.

working with a D.P. of four cells at least sixteen were really in use. Throughout these experiments they were maintained at a temperature close to 15° C., by a regulator which warmed the tank when below 15° C. and turned tap-water through the tank when above 15° C. As full particulars are given in the pages of Paper J., I think the above summary will be sufficient.

There is one alteration in the electrical connections to which I wish to draw attention. In former experiments some time always elapsed, after the current was established, before any observations were taken. It, however, appeared probable that in this work I should occasionally have to cut off and put on the current during an experiment. For some time after the establishing of the current, a constant re-adjustment of the rheochord was required, as the temperature of the wires, &c., forming the external circuit was gradually raised, and the external resistance in consequence increased. During this period of adjustment the balance could not be as accurately maintained as when the temperature of the external wires had become steady. In order to avoid this preliminary adjustment, a coil of the same wire and resistance as that in the calorimeter was constructed and placed in a tube containing the same oil as that in the calorimeter, and this tube was fixed in the tank at F (Plate 6, fig. 3).

At k_1 a key was so arranged that one movement brought the storages into connection with the calorimeter coil by means of leads 2 and 4, while another movement caused the current to leave the calorimeter circuit and pass through F. A second key (not shown in fig. 3) enabled the Clark cell to be also connected to F. The current was sent through F for 10 minutes or so and the balance adjusted, before an experiment commenced. On moving the key at k_1, the current was switched on to the calorimeter, the Clark cell circuit was then also shifted and the balance once more made perfect. Thus the current through the externals was kept constant whether it was passing through the calorimeter or not, and therefore the rheochord required far less manipulation.

Again, the key k_1 was so arranged that whenever the current was shifted, a connection in a chronograph circuit was established, and thus the times of "making and breaking" the calorimetric current were automatically registered. True, the marked time was in each case a fraction of a second before the "make and break," but the actual duration of the intervals was truly recorded.

Measurement of R_1.

The holes in the paraffin blocks P_1 and P_2 (Plate 6, fig. 3) contained mercury. Connection could be made by two cross pieces of copper rod, between either of the slots in P_1 and any of the holes in P_2. These copper rods, when in position, rested on the wires which passed through the bottom of the holes. Denoting the resistance of the coil by R_1, that of the leads from P_2 to the lid of the calorimeter by r_1, r_2, r_3, r_4, it is evident that by a movement of the connecting rods, the following resistances could be taken, viz.:—

$$r_1 + r_2, \quad r_1 + R_1 + r_3, \quad r_2 + R_1 + r_4, \quad r_3 + r_4.$$

If N_1, N_2, N_3, and N_4 are the resulting numbers, we get

$$R_1 = \{(N_2 + N_3) - (N_1 + N_4)\}/2,$$

and there is no necessity that r_1, r_2, r_3, and r_4 should be equal. The value of R_1 was always obtained in the above manner, and then expressed in terms of the box ohm at 17°. A full account is given in Paper J., pp. 407–410, of the comparisons of the individual coils of my resistance box with the B.A. Standards, and the values of R_1 were reduced to true ohms in the manner there indicated, with the further corrections given in a later communication.*

In Appendix III. I give an example of an observation together with the reductions.

It was next necessary to find the increase in R_1 (δR) due to the rise of temperature caused by the current. This was done in substantially the same manner as that described in Paper J., pp. 404–407 ; δR was in this case found to be very small—as shown by the following table.

TABLE VII.

Potential difference in terms of a Clark cell.	δR.
1	·00076
2	·00198
3	·00377
4	·00630

The resulting curve was (as in other similar cases) practically a parabola.

A further correction was necessary for the heat developed in leads 2 and 4 in the portion that passed from the steel to the calorimeter lid. Their total resistance was ·0068. We may assume that half the heat here generated passed into the calorimeter, and therefore consider their resistance as ·0034 ohm $= r$. Now the points kept at a constant D.P. were between these wires and the coil, and since $JH = E^2/R\,(1 + r/R)\,t$, we get the effective resistance $= R - r$.

The following table gives the values (after the application of all corrections) of R_1 at the temperatures at which the L experiments were performed, the potential difference being denoted by the suffix.

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* 'Roy. Soc. Proc.,' vol. 55, p. 25.

TABLE VIII.

Temp.	R_0.	R_{2e}.	R_{3e}.	R_{4e}.
° 20	10·3246	10·3266	10·3284	10·3309
30	10·3482	10·3502	10·3520	10·3545
40	10·3720	10·3740	10·3758	10·3783
50	10·3966	10·3986	10·4003	10·4028

δR_1 per 1° C. = ·0024.

This coil has shown no signs of any change throughout its history.

As $Q_e = (ne)^2/R_1J$, I have now indicated how the value of Q_e could be accurately ascertained.

Had full details of the method not been given in previously published papers, it would have been necessary for me to give further particulars as to the various measurements.

There can, I think, be little doubt that the value of Q_e could be determined with great certainty.

I have already (see p. 272 *supra*) pointed out that even if my value of J ($4·199 \times 10^7$) be in error, it is the correct value to use for these experiments, and that even if e (the D.P. of a Clark cell) and the units in which R_1 is measured (*i.e.*, the value of a "true ohm") are in error, the results are unaffected, provided that no changes have taken place in my Clark cells, or the coils of the resistance box since they were used for the determination of the value of J.

[Note, May 4, 1895.—During the spring of this year my Clark cells were carefully re-compared with the Cavendish standard, R I. Comparisons were made at regular intervals, and Mr. SKINNER was so kind as to take some independent observations. The differences are expressed in hundred-thousandths of the E.M.F. of the standard. The highest of the thirty cells exceeds R I by 40 such units. The lowest is less than R I by 36. The mean value of the whole set is less than R I by 3 such units (*i.e.*, by 0·00004 volt). Thus, although the individual cells show larger discrepancies than in 1892–4, the mean value is almost exactly that of the Cavendish standard. The previous history of that standard shows that it had remained unchanged during the interval of eight years which had elapsed between the absolute determination of its E.M.F. by Lord RAYLEIGH in 1883, and that by Messrs. GLAZEBROOK and SKINNER in 1891. There is no reason to suppose that it has altered since the latter date, and this conclusion is borne out by comparison with other standards at the Cavendish Laboratory. I think, therefore, that I am justified in assuming that the mean E.M.F. of my cells remains practically unaltered.

Cells 37 to 42 have been compared at Manchester by Professor SCHUSTER with his standard. These six have the highest mean E.M.F. of any of my sets. Their mean value exceeds R I by 22 units, and they exceed Professor SCHUSTER's standard by

70 units. It would thus appear that R I exceeds Professor SCHUSTER'S standard by 48 units, *i.e.*, by about 0·0007 volt. It must, however, be remembered that between these comparisons the cells had been subjected to several transits by railway.]

Measurement of Time.

The chronograph was controlled by the electric clock described in Paper J. (p. 414). The clock has remained untouched from July 16th to the present day—November 18th, and during that time it has gained 12 minutes, *i.e.*, a gaining rate of about 1 in 15,000. The gain has been regular throughout the interval, the clock being singularly indifferent to small changes of temperature. I therefore consider that the measurements of time require no correction.

Section IX.—THE RESULTS OF EXPERIMENTS IN WHICH EVAPORATION WAS PROMOTED BY THE PASSAGE OF A GAS.

I have hitherto referred to the experiments I describe in this section as "preliminary" for want of a better name; but I had originally hoped that the method would have given satisfactory results. Although these experiments have had but little influence on my conclusions, I will briefly describe them, as I am yet at a loss to account for their comparative irregularity.

Dry air, or other gas, was forced in a continuous stream through the water to be evaporated; the cooling thus caused was balanced as before described, and the weight of water evaporated determined by the increase in weight of drying bulbs. I wished to adopt this method, because by adjusting the flow of air the rate of loss of heat could be (by proper arrangements) regulated with nicety, and the thermal balance maintained with great accuracy. When water is made to boil by diminished pressure, the regulation of the cooling presents many manipulative difficulties that I was anxious to avoid.

The experiments were conducted as follows. About 20 cub. centims. of water were placed in the flask F (Plate 6, fig. 1),* the water force-pump set going, and the air first passed through the H_2SO_4 bottles and "tower" S, then through the U-tube and drying tower P—both containing P_2O_5. It then passed through the 3-way tap (T_2) into the 30-feet copper coil (C_1) in the tank water, thus attaining the temperature θ_0 of the tank, and after traversing the immersed tap T_3, bubbled through the water in the silver flask. The air and vapour now rose up through the 18 feet of silver coil (C_2) within the calorimeter, passed out through the 4-way tap (T_4), which was opened in such a manner as to direct the air current into some H_2SO_4 bulbs (not

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* This figure is diagrammatic only, and conveys no idea of dimensions or actual position. For example, the coil C_1 surrounded the steel vessel, and the 4-way tap T_4 was on the same side of the apparatus as the tap T_2. The pipes, &c., crossed and re-crossed each other in such a manner as to render any direct representation impossible. The drying bulbs and connections are not indicated in the figure, as they were afterwards replaced by the condenser (B) and manometer (M_2).

shown in figure) containing the same depth of H_2SO_4 as the bulbs to be weighed. Thus when T_4 was afterwards so turned as to change the direction of the current to the weighing bulbs, no alteration took place in the rate of flow, which was adjusted as required in the following manner. A T-piece (not shown in sketch) was inserted in the tube between the drying tower P and the tap T_2. The vertical leg of the T-piece was a wide graduated tube, open at its lower extremity, and immersed in a deep, narrow vessel (a hydrometer jar) filled with H_2SO_4. If the air pressure within the pipes was greater than that due to the column of H_2SO_4 above the open end of this leg, the excess of gas bubbled up through the H_2SO_4 and escaped into the open air. Thus by raising or lowering the vessel the pressure and quantity of air passing through the whole apparatus could be regulated with exactness. I found it possible to so adjust the flow that when the heat supply was Q_e and Q_s, the galvanometer showed no change for nearly an hour. A further advantage of this arrangement was that I could close any tap without increasing the pressure within the apparatus, the whole of the gas then passing out through the regulator. The pressure of the gas near the flask was read on the manometer M_1, which had two wide bulbs near the base, the mercury filling the lower bend and three-quarters of the bulbs. The narrow tube on the scale side contained water resting on the mercury, and thus a very open scale was obtained. The instrument was carefully standardised, and a movement of 7·78 centims. in the water level corresponded to a change in the pressure of 1 centim. of mercury. The water was completely cut off by the mercury from all communication with the gas tubes.

The electric connections having been made and the rheochord adjusted until the high resistance galvanometer (G_1) showed that the D.P. at the ends of the coil was that of the Clark cells (I shall speak of this hereafter as the "electric balance," and of the adjustment of the loss or gain of heat as the "thermal balance"), the gas flow was then diminished until the platinum thermometer galvanometer showed that θ_1 slightly exceeded θ_0 (θ_1 = calorimeter temperature, θ_0 = temperature of surrounding walls). The current was then switched on to the alternative coil F (fig. 3), θ_1 now decreased and at the moment when $\theta_1 = \theta_0$ the current was switched back again, the key itself recording the time on the chronograph tape. About the same time, the 4-way tap T_4 was turned so as to cause the escaping gas to pass through the weighing bulbs. This time had not to be recorded, nor was there any necessity that it should be nearly or at all coincident with the time of establishing the electric current. If, however, θ_1 did not exactly equal θ_0 at the moment of turning T_4, the swing of the galvanometer was recorded and the tap only closed at the end of an experiment when the swing was identical with the initial one.

When necessary the thermal balance was maintained for 1, 2, or, in some cases, 3 hours by adjusting the flow of gas. At the close of an experiment θ_1 was again allowed to rise slightly above θ_0, the current switched off (again itself recording the time) and as θ_1 descended the tap was turned back to its old position when $\theta_1 = \theta_0$, or when the swing was the same as the initial one. The taps T_2 and T_4, were then turned so that the dry air instead of passing through the tank, &c., went straight through T_4 to the weighing bulbs, and thus any moisture left in the connecting tubes was swept into the bulbs.

The swing of the galvanometer was rarely as much as 50 (indicating a difference of about 0°·01 between θ_1 and θ_0) throughout one of these experiments, and when such oscillations occurred care was taken to alter the adjustments so that a swing to the right was invariably followed by a similar swing to the left. The whole apparatus could easily be managed by two observers and, on occasions, it was unnecessary to make an alteration of any kind for half-an-hour at a time.

As before stated, the stirrer automatically recorded on the chronograph tape the time of each 1000 revolutions.

The weighing bulbs were of peculiar construction and specially designed for this work. The gas passed through four washings of H_2SO_4 and then through a tube of P_2O_5, on the further side of which was attached a $CaCl_2$ tube. The latter was not included in the weighings, but only used to prevent any access of the laboratory air to the P_2O_5 when the gas current was not passing. The weighing bulbs were connected with the exit tube by a mercury trap* and had simply to be lowered into place, no fitting of rubber tubes being necessary. To avoid condensation, the mercury trough and also the whole of the exit tube exterior to the tank were maintained at a temperature above θ_0 by means of small gas jets.

At the close of an experiment the weighing-bulbs were removed (with their precisely similar tares) to the balance case. A careful weighing was made about an hour after the experiment, and again next morning; an apparent increase of about ·0005 gram generally presenting itself.

As (especially in the stirring experiments) small differences in weight had to be measured, I took every precaution I could devise, and I also followed the suggestions of friends whose experience in this matter was greater than my own. The balance was a short-beam one by VERBECK and PECKHOLDT, and was constructed so as to give a swing of 2·5 divisions per 1 milligram when loaded up to 500 grams. The actual weights to be measured were about 120 grams. I made special efforts to keep the temperature of the balance case steady, and noted the effects of changes in temperature on the ratio of the arms, etc.

The weights used were by Messrs. OERTLING, and re-standardised by them last year.

The increase in weight during the electrical experiments varied from ·8 to 3·5 grams, the increase during the stirring experiments from ·06 to ·08 gram.

I think it certain that the weighing error was never so much as ·002 gram, and it was probably much less; thus I do not believe that any discrepancies in the values of L greater than 1 in 1000 can be due to errors of this description.

As before described (p. 291) the mass of water evaporated by the stirring supply was

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* Neither bulbs nor trough are shown in fig. 1, Plate 6.

determined in a similar manner. Thus, if m_s be the mass evaporated per second by the stirrer, we have (using the same notation as before)

$$\mathrm{ML} - m_s t_s = \mathrm{Q}_e t_e + \Sigma q.^{*}$$

I spent some weeks over these experiments, but the results were so uncertain, that at last I was compelled to give up all hopes of attaining my object by this method. I will therefore omit details and give results only.

TABLE IX.—Evaporation Caused by Passing Dry Gas.

Date.	Number of Clark cells.	Temperature.	L.	Remarks.
September 2	2	49°·54	567·5	Calorimeter filled with aniline
,, 2	3	49·54	564·4	
,, 11	1	50·01	566·6	,, ,, ,, oil
,, 11	3	50·00	566·3	
,, 11	2	50·00	567·8	
	Mean .	49·82	566·5	
August 29	2	39·98	576·9	Calorimeter filled with aniline
,, 29	1	39·97	572·2	
,, 31	2	39·98	574·5	
,, 31	1	39·98	572·9	
September 2	1	39·99	569·8	
,, 2	2	39·99	572·9	
,, 2	1	39·98	569·9	
,, 12	3	40·01	572·2	Oil in calorimeter *Nitrogen passing
,, 12	2	40·00	569·4	
,, 13	2	39·98	572·7*	
	Mean .	39·99	572·4	
August 19	1	24·97	582·6	*Nitrogen passing Calorimeter filled with aniline
,, 19	1	24·96	580·6	
,, 20	1	24·96	584·2	
,, 22	1	24·96	581·7*	
,, 24	1	24·97	580·0	
,, 24	1	24·97	584·7	
,, 27	1	24·95	581·5	
,, 27	1	24·95	580·3	
,, 28	1	24·95	581·4	
	Mean .	24·96	581·9	

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* Σq in this case $= \mathrm{C}_{\theta_1}\{(\theta'_0 - \theta''_0) + (d' - d'')\} + \mathrm{C}'_{\theta_1}(\mathrm{T}' - \mathrm{T}'')$ where C'_{θ_1} is the "mean mass" of the water in the flask, and T′ and T″ the initial and final temperatures of that water as indicated by the flask thermometer G_2.

I have included in the above table all the experiments with the exception of two, which were performed on the same day (September 3rd), and whose extreme divergence from the others led to the discovery that the insulation of one of the leads had fallen off. In consequence, the value of R_1 was uncertain. Between September 3rd and 11th the whole apparatus was taken to pieces and fitted with new leads and insulators. From this time onwards the calorimeter was filled with oil in place of aniline (see Paper A., p. 77).

I think it is evident that the discrepancies are greater than can be accounted for by errors in weighing, as they sometimes amount to nearly 1 per cent.

I at first suspected that some moisture was escaping uncaught by the weighing bulbs, or that the entering air was not dry. I believe, for two reasons, that this was not the case. (1) The P_2O_5 bulb, through which the gas finally passed, in no case increased in weight by as much as 0·0040 gram, and usually only by about 0·0020 gram, which showed how completely the moisture had been removed by the H_2SO_4. (2) Before entering the apparatus the gas passed also through H_2SO_4 and P_2O_5, therefore any quantity of moisture which escaped these drying agents would be likely to also escape the similar agents at the exit end, and thus would not affect their weight. I had good evidence that this was the case, for I thoroughly dried the flask and tubes at a temperature of 40°, and then passed the gas through the apparatus into the weighing bulbs for an hour and a half; but the increase of weight in that time was not as much as ·0005 gram. Again, if the gas was more completely dried at one end than at the other, the effect would have been to make all the values of L too low or too high. Of course, I was entirely in the dark at the time of these experiments as to the real value of L, but I now find that the mean of each group gives a close approximation to the true value, hence there was no permanent raising or lowering cause at work.

It will be noticed that the rate of flow of air was greatly changed during these experiments; when three cells were used the rate of evaporation had to be nine times as great as when the D.P. was that of one cell. Inspection of the table will show that the variations in the values of L do not appear to be functions of the rate.

For some time I fancied that "priming" might be taking place, but, if so, the experiments with a rapid flow would probably all have given lower values than those with a slow flow, the carrying of particles of unevaporated water being much more probable when the velocity of the gas current was increased nine times.

Again, it has been suggested that, as the pressure of the gas diminished during its passage through the apparatus, some heat would in consequence disappear. I would point out that the only constricted portions of the passage (after the air had once entered the tank) were within the calorimeter, and, if all the work done by the gas was performed within the calorimeter, the cooling, owing to expansion, would be just balanced by the warming of the tubes at the constricted points. Also, a persistent lowering of the values of L would be caused, and (as above pointed out) I now find that such is not the case. To test this matter at the time, however, I observed the rate of rise due to the "stirring supply"—firstly, when no air was passing; secondly, when the air was passing through the *dry* flask and tubes and I could detect no difference.

So long as the thermal balance is maintained with the same potential difference, the rate of evaporation must be the same, whatever method is adopted. I cannot see that the external work to be done is likely to alter because the space above the water is de-saturated by passing a gas instead of removing the saturated vapour by an exhaust, and this view is borne out by the close agreement between the means of those groups and my later experiments.

There is one curious fact which may possibly throw some light on the matter. I performed two experiments (August 22 and September 13), passing nitrogen instead of air. Of course I had at that time no means of judging of the comparative value of the different experiments, and therefore was ignorant of the close approximation of the nitrogen values and my final ones. Had I then been aware of the coincidence, I should have continued the nitrogen experiments in order to ascertain if the agreement was fortuitous.

The close agreement is shown in the following table:—

TABLE X.

Temperature.	Results of nitrogen experiments.	Final values.
24°·96	581·68 (1 cell)	581·73
39·98	572·72 (2 cells)	572·69

When time allows, I propose to repeat these nitrogen experiments, in the hope that some light may thereby be thrown on the matter; in the meantime, I am unable to suggest any sufficient explanation of this phenomenon.

Section X.—THE METHOD FINALLY ADOPTED. "EXHAUST" EXPERIMENTS.

A study of the results obtained from the experiments described in the last section led me to the conclusion that it was necessary to seek some other method of attacking the problem. I have not described many of the precautions I gradually adopted during those experiments, but since none of them had produced any appreciable improvement it was evident that the real cause of the irregularities had not been ascertained. Even the entire change involved by the replacement of aniline by oil, the removal and refitting of the calorimeter, &c., appeared to have had no effect of any kind.

I determined, therefore, to adopt an alternative method of producing evaporation, viz., by reducing the total pressure below the pressure of the saturated vapour. It possessed the following great advantages: (1) there would be no necessity for the passage of gas through the apparatus, (2) the weighing-bulbs, &c., for catching the aqueous vapour could be dispensed with. I was, however, reluctant to adopt this method, for I anticipated that several practical difficulties would present themselves; for example, it would be necessary to insert a known weight of water into the flask, and continue the experiments until the whole of that water was evaporated, thus I should not be able to finish the experiment at any time when $\theta_1 = \theta_0$, as was the case during the "pressure" experiments.

It would also be more difficult to maintain the thermal balance at such perfection as in the former experiments, for it would be less easy to control the rate of evaporation.

Again, when air was passing through the apparatus, the water in the flask was efficiently stirred and its temperature in consequence approximated closely to that of the calorimeter, even when the rate of evaporation was rapid. A thermometer (G_2) was, during the preliminary experiments, placed as described in Section V., with its bulb near the bottom of the flask, and I found that the difference in temperature between the flask water and the calorimeter liquid did not, in the greatest case, exceed 0°·15 C. If no gas was passing, the water would not be stirred, and it appeared probable that the difference in temperature might greatly exceed this amount. In this case not only would the observed temperature (θ_1) exceed the real temperature of the water, but also the vapour when escaping through the coil would abstract heat from the calorimeter, and thus (as pointed out by WINKELMANN in his criticisms of REGNAULT'S experiments) the resulting value of L would be too great.

It did not appear possible to determine the interior flask temperature accurately by means of a mercury thermometer, whose bulb was placed in a chamber where the pressure was reduced to something between 10 and 100 millims., and if I placed a platinum thermometer in the flask, a third electrical circuit and galvanometer would have had to be added with a third observer to read the indications—additions which circumstances did not render possible.

I did not feel that it would be of any use to adopt REGNAULT'S method of determining the temperature by the vapour pressure (see Section II.), and I endeavoured therefore to find some means of preventing the temperature of the evaporating water from falling below that of the walls of the flask.

It was evident that the smaller the quantity of contained water, the more nearly would its temperature approximate to that of the surface upon which it rested. If it was possible to discharge the water drop by drop on to the silver surface, the difference in temperature would probably be negligible, and after some trials I found a method of effecting this. A glass tube, exactly fitting into the communicating tube *h h'* (Plate 5, fig. 1) was closed at one end, the other end being drawn out so that it would pass through the constriction at the calorimeter lid (see p. 279), and the narrow tube which thus projected into the flask, terminated in a very fine opening.

A tube of this kind (which I shall call a "dropper") is shown in place in Plate 5, fig. 1. It was filled with water in the same manner as a "weight thermometer." To ascertain its action, I placed it within a wide glass tube whose lower end was closed. A constriction in the wide tube enabled me to stand the "dropper" within it, so that the narrow portion projected downwards (without touching the bottom) in the same manner as it would do when *in situ* above the flask. The upper end of the enclosing tube was connected with the exhaust pumps, a clamp being fixed on the connections. I found that when the pressure fell below that of the aqueous vapour, the water in the dropper was discharged into the surrounding chamber in a succession of small drops, but that if the communication with the exhaust was closed the dropping ceased. If the vacuum was maintained, the drops first thrown on the walls disappeared while a fresh supply was ejected. I concluded that when the space was absolutely saturated there was equilibrium, and I found that the disturbance of that equilibrium, caused by an almost imperceptible decrease in the pressure, was sufficient to maintain the flow. The size of the orifice of the dropper did not appear to be of any consequence, as I ascertained by experiment. Of course a certain amount of water-vapour must have been formed to saturate the space left within the dropping tube as the water retreated. It is evident, however, that the quantity thus evaporated would be very small. At the highest temperature at which I have yet worked (50° C.), the specific volume of water-vapour is somewhat below 12,000, and as the volume of the droppers used did not exceed 4·1 cub. centims., the weight of water required to saturate this space would be about ·001 gram, and at lower temperatures much less. The greater portion of the heat required for such evaporation must, however, have been taken from the calorimeter, for the shoulder of the dropper rested on the metal ring at the base of the tube *h h'* (Plate 5, fig. 1), and this ring formed a portion of the calorimeter. In order to make certain of this matter, I lowered the filled dropper into place, the contained water being slightly cooler than the calorimeter temperature, and deduced its water equivalent in the manner described in Appendix II., where I show how the capacity for heat of the thermometer (G_2) was ascertained. The weight of water and glass in the dropper being known, its water-equivalent could also be alternatively obtained by calculation. It was difficult to accurately ascertain the temperature of the dropper just before lowering it into place, but the experimental results were in practical agreement with the calculated ones, and heat which disappeared within the dropper must therefore have been taken from the calorimeter.

It is thus evident that no correction is rendered necessary by this internal evaporation.

The adoption of the exhaust method involved certain changes in the exterior connections. The weighing bulbs and mercury trap were replaced by the bottle B (Plate 6, fig. 1). The connecting tubes which passed into this bottle were ground to fit and no corks were used. The calorimeter exit tube did not dip into the H_2SO_4 but terminated about an inch above the surface of the acid. The manometer gave (after comparison with the barometer) the pressure of the vapour in the condenser. The tube H branched into two; one was connected with a water pump, by which the pressure could be brought down to about 20 millims., and the other with a GEISSLER's mercury pump.

Description of an Experiment.

The dropper was filled by alternate boiling and cooling,* and was allowed to stand in a vessel of warm water until the temperature had fallen to about 5° above that to which it was to be exposed during the experiment. After removal from the water it was thoroughly dried externally and placed in a short glass tube closed at both ends by rubber corks, a precisely similar tube closed in the same manner being used as a tare. The case and dropper when full weighed about 20 grams.

The dropper was always filled some hours before an experiment and placed in the balance case until wanted. After the tank temperature had become steady the dropper and its case, having been weighed, were placed within a larger tube immersed in the tank water.

The connections of the electric circuit having been completed, the calorimeter temperature (θ_1) was made coincident with the tank temperature (θ_0), the current being then switched on to the alternative coil, and thus (as previously explained) the temperature of the external resistances was kept steady, even when the current was not passing through the calorimeter. The dropper and case were then removed from the tank, a silk thread was passed through a platinum loop, fused into the top of the dropper, and it was lowered into its place at the bottom of the tube *h* (Plate 5, fig. 1). The thread was withdrawn and an air-tight piston, consisting of a section of a rubber cork mounted on a glass rod, was thrust down *h* until it arrived at the top of the dropper. A slightly larger conical rubber cork, mounted on the same rod, closed the top of the tube *h*, therefore all diffusion or evaporation up the connecting tube was prevented, and no difficulty was experienced in closing it in such a manner as to be absolutely air-tight.

It was necessary to delay the commencement of the experiment until the dropper and contained water had assumed the temperature of the calorimeter (θ_1). This took some time, although the temperature of the former must (owing to the previous immersion in the tank) have been very nearly θ_1. Observation of the thermometer-galvanometer gave the extent of the cooling caused by the introduction of the dropping tube. The current was then switched on until θ_1 again equalled θ_0, the galvanometer was observed, and the process repeated until no further cooling effect was visible.

It appeared possible that slight evaporation through the fine opening of the dropper might during this interval be the cause of some cooling, and I was for a time very

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* I found that it was necessary to fix a small capillary tube within the dropper, otherwise the contained water refused to start boiling when the external pressure was removed.

uneasy about this point. I found, however, that if the tube, after filling and weighing, was placed in a desiccator for 12 hours with the opening uncovered, the loss of weight was less than 0·005 gram; it was, therefore, not probable that any appreciable evaporation took place during the interval occupied by the temperature adjustment. Again, the dropper, after being filled, was removed from the beaker at a higher temperature than that of the tank, so that immersion in the calorimeter would not lead to the expulsion of any water, provided that the small air-bubble formed at the lower end when the dropper was cooled in the balance case did not rise into the upper part of the instrument, in which case the re-heating would possibly cause a small expulsion, owing to the warming of the air-bubble, which was previously absent from the tube. I think it just possible that this happened in some of the earlier experiments (Nos. I. to V.), but, after No. V., I adopted a new form of tube, of which the lower end was first turned up for about 1 centim., and then bent at right angles. Thus any air-bubble formed during the cooling remained at the open end, and also the water, when ultimately expelled, was thrown against the side of the flask (see Plate 5, fig. 1).

The results of experiments performed after this alteration are in closer agreement than preceding ones.

When θ_1 was found by observation to have become quite steady, the contact-maker of the bridge was carefully adjusted to the bridge null-point (see p. 288), and the swing (if any) of the galvanometer was read. If θ_1 was found to be lower than θ_0, a further adjustment was made. In cases where θ_1 slightly exceeded θ_0, no adjustment was possible without again removing the dropper, so, unless the difference was considerable (*e.g.*, a swing exceeding 50 or 60, that is, a difference of about 0°·01 C., see Table V., *supra*), the experiment was proceeded with. Three observations were taken of the swing, and the chronograph tape was marked during the second observation. This gave the commencement of the interval of time t_s, *i.e.*, the time during which the stirring supply had to be estimated.

The pressure in the condenser B had been previously brought down below that required during the experiment, and, immediately after the observer at the galvanometer had registered the swings, the tap T_4 was opened. The manometer M at once showed an increase of pressure, due to the air in the flask and tubes expanding into the condenser. The expansion of this air produced a visible cooling effect, causing a galvanometer swing of about 90—equivalent to nearly 0°·02 C. (Table V., *supra*). The manner in which this loss of heat was compensated for will be described later.

The water pump having been cut off by the tap T_6, the mercury pump was if necessary brought into action. The moment at which the discharge from the dropper commenced was indicated with great accuracy by the galvanometer and announced by Observer No. II. The electric current was at once switched on to the calorimeter circuit (the action recording itself on the chronograph tape) and the electric balance, if not perfect, immediately adjusted by Observer No. I. Owing to the alternative-circuit method previously described, only a very trifling adjustment was as a rule required. Observer I. had now to direct his attention to the maintenance of the thermal balance. This, as I have anticipated, was found at first to be matter of some difficulty, but practice rendered the task comparatively easy.

The discrepancies observable in the earlier experiments (Table XI.) are, I expect, in some measure due to fluctuations in the value of θ_1. As a general rule, the evaporation at the start was too rapid, the pressure having been too much reduced by the last stroke of the pump—the galvanometer swing amounting to as much as -500 or -600 (nearly $0^\circ\cdot1$ C.). The tap T_4 was closed and (evaporation being thus prevented) the electric current was allowed to raise θ_1 until the $+$ galvanometer swing announced by Observer II. was about equal to the previous negative swing; the time occupied by these two large oscillations being only a minute or two. T_4 was then partially opened until it was found that θ_1 was slowly falling. When θ_1 became equal to θ_0 the rate of cooling was further decreased and during the remainder of the experiment the galvanometer swing (which was called aloud by Observer II. every 15 or 20 seconds) rarely exceeded 50 or 60 (*i.e.*, about $0^\circ\cdot01$ C.) and in many cases the difference between θ_1 and θ_0 did not exceed $0^\circ\cdot002$ C. in the course of half-an-hour.

As the whole of the aqueous vapour passing into the condenser was not at once absorbed by the H_2SO_4, the pressure slowly increased, and thus gave a further power of adjustment. The large bulb of the Geissler was kept vacuous and thus, by opening the tap T_7 the pressure in the condenser could at any time be decreased. By one rapid turn of the tap an almost imperceptible rise of the manometer M was caused, and a very slight difference in pressure produced a considerable alteration in the cooling rate; thus, if θ_1 was rising, a single revolution of the tap T_7 would check the rise, another revolution would probably give the cooling a slight mastery. The operations by which the thermal balance was maintained may, as I have described them, appear both cumbersome and difficult. I can only say that (after the first three or four experiments) the control was nearly perfect and a single oscillation of as much as $0^\circ\cdot01$ C. would have been considered excessive. From beginning to end of each experiment great care was taken that each positive oscillation should be succeeded by a corresponding negative one.

The electric balance was also maintained by Observer I.; but as the temperature of the coil did not appreciably alter throughout, this balance required but little attention.

The taps T_4, T_6, T_7, and T_2, as well as the handles of the rheochord and all the electric keys, were so placed as to be within reach of Observer I. without change of position. The high resistance galvanometer screen was immediately in front of him, and also the manometer, M, whose readings were constantly observed. Near the commencement and end of an experiment the physical strain was great, but when both thermal and electrical balances had been finally adjusted there were often intervals of more than ten minutes when no alterations had to be made.

From beginning to end, the task of Observer II. was that of announcing the galvanometer swings—a monotonous and uninteresting operation, which, however, required constant attention.

When the experiment was approaching its termination a close watch had to be kept, for, unless the current was switched off the instant a sudden rise showed that all the water had been evaporated, the lapse of a few seconds would have raised θ_1 considerably above θ_0. If, on the other hand, the current was turned off too soon, it was always possible to switch it on again and raise θ_1 up to θ_0. After the first experiment it was easy to calculate (knowing the weight of the empty and the full dropper) the approximate time of ending. As a rule I cut off the current two or three seconds before that time, then increased the vacuum considerably to make sure of evaporating off the last drop of water, again established the current, and brought θ_1 to just *below* θ_0, repeating this process as often as necessary—all the actions recording themselves on the chronograph tape. When θ_1 had become absolutely steady, or only showed the slight increase due to the stirring, it was safe to assume that all the water had been evaporated.

The tap T_4 was then finally closed, the tap T_3 slowly opened, and the air from the drying bottles S and P allowed to pass in through the 30-feet coil, C_1, in the tank. The increase of θ_1 caused by the compression of this air was found, by observation, to be the same as the depression (previously referred to) which took place during exhaustion, and it was to allow for this rise that θ_1 was set slightly below θ_0. When the internal and external pressures had become equal, T_3 was closed and the current again switched on if necessary, until the swing became the same as the initial swings. If, however, θ_1 exceeded θ_0, this was not possible, and a correction had afterwards to be made for any difference.

After repeated observation had shown that θ_1 was steady, Observer II. read, as before, three galvanometer swings, pressing his chronograph key at the middle one. This record gave the termination of the interval t_s, the time during which the stirring heat had to be estimated.

It will be seen from the preceding account that t_s always considerably exceeded t_e, the time of electrical supply.

The plugs closing the tube *h h′* (Plate 5, fig. 1) were now withdrawn, a wire ending in a hook passed down the tube, the dropper extracted by means of its platinum loop, and immediately returned to its case, which was at once corked and placed on the balance, and afterwards weighed, with the various precautions previously referred to.

The only remaining operation was that of translating the chronograph tape which gave the value to $\frac{1}{10}$ second of t_s, t_e, and the time of each thousand revolutions of the stirrer.

Remarks on Tables XI. to XIII.

Tables XI., XII., and XIII. give the experimental results; Table XI. those at temperatures approximating to 40° ; Table XII. those at temperatures near to 30° ; and Table XIII. two experiments at 30°, where the rate of evaporation was but $\frac{9}{16}$ of the former rate. Any inaccuracy in the values of Q_s, t_s, and Σq would in these last experiments tell with double force. Also, the rate of evaporation being so greatly diminished, it was probable that any depression of the temperature of the evaporating water below θ_1 would be about half of what it was when four cells were used, and thus the magnitude of any error, caused by such depression, would be indicated.

Had time permitted, I should have repeated these experiments with a still slower rate of evaporation. I was, however, surprised to find that it was more difficult to maintain the thermal balance with the lower than with the higher D.P.

A large number of differently shaped and sized " droppers " were used, hence the difference in the values of M.

As I preferred to alter the conditions as much as possible, no effort was made to keep the stirring rate the same for different experiments.

In most cases the droppers when removed after an experiment appeared to be absolutely dry. In two cases, however, some signs of moisture were visible. I am at a loss to account for this, as I feel sure that evaporation had ceased, and that there was no water left on the surface of the silver flask. The moisture thus remaining was, of course, included in the final weighing, and would not therefore introduce any error provided the *flask* was dry. It is noticeable, however, that the two experiments at the end of which this moisture was visible (Nos. V. and IV.) give, as shown by Table XI. (*b*), the highest values for L.*

The value of $d' - d''$ will be noticed as unusually high in No. I. Here we had no idea of the time when the experiment would finish, and did not allow for the rise in θ_1 caused by the introduction of the dry air at the end, hence the close of the experiment found θ_1 too high by nearly 0°·028 C. Also we could only approximate to the value of t_s, having in the hurry of the initial experiment forgotten to mark the time of finish. The remembrance of a casual observation of the clock, however, enabled us to fix it approximately. An error of 100 seconds in t_s would in that experiment produce an error of not quite $\pm$ ·25 in L, and the value assigned to t_s is probably within a minute of the truth.

During Experiment II. a portion of the mercury covering the core of tap T_3 became, owing to careless manipulation, sucked into the apparatus, and in some unexplained manner stopped the evaporation for nearly ten minutes, during which the electric current had to be switched off. However, the accident had but little effect on the resulting value of L.

No. XI. was an almost perfect experiment, the thermal balance being maintained very closely throughout. I do not think that the variations in θ_1 during this experiment at any time amounted to 0°·005 C., and the external temperature (θ_0) remained,

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* Even when the same dropper was used, and the bulb was afterwards found to be dry, the values of M were not identical. The mass of contained water depended on the temperature of the dropper when removed from the beaker after filling, and as the beaker was only roughly brought to a temperature somewhat above θ_1, the values of M varied.

as shown by Col. III., absolutely unchanged. It is noticeable that its result (Table XI. (*b*)) is almost exactly the mean value of Experiments VI. to XII.

I have included in these tables every experiment performed by the exhaust method with the exception of one, during a portion of which the chronograph ceased to mark, or rather marked continuously. Both accident and its cause were only discovered at the end of the experiment, when it was found that a loose piece of wire had short-circuited the chronograph circuit.

Notation used in Tables XI. to XIII.

Col. I. Number of experiment and date.

,, II. Temperature of the experiment (θ_0) on the nitrogen scale.

,, III. m_1 the initial mass of dropper and contents, m_2 the final mass; hence $m_1 - m_2 =$ mass evaporated $=$ M.
(M is in all cases the weight corrected to *vacuo.*)

,, IV. Time (in seconds) during which the electric current was passing through the calorimeter $= t_e$.

,, V. Time t_s (in seconds) during which the stirring supply of heat was maintained. $t_s =$ duration of experiment.

,, VI. Number of revolutions per second of the stirrer $= r_1$.

,, VII. Difference $(\theta'_0 - \theta''_0)$ between the initial (θ'_0) and final (θ''_0) temperature of the surrounding walls. This is expressed in the nitrogen scale, the value of each millimetre of thermometer II. having been previously determined by the comparison referred to in Section IV.

,, VIII. Let θ'_1 (initial calorimeter temperature) exceed θ'_0 by d', and let θ''_1 (final calorimeter temperature) exceed θ''_0 by d''.
Then this column gives value of $d' - d''$ deduced from the galvanometer swings by Table V., Section VI.

,, IX. Gives the capacity for heat of calorimeter and contents (C_{θ_1}) at the temperature of the calorimeter θ_1 (Table III.).

,, X. The temperature of the Clark cells during the experiment.

,, XI. The value of R_1 at temperature θ_1 from Table VII., Section VIII.

,, XII. The average pressure (p'') in the condenser during the experiment (in millimetres of Hg).

,, XIII. The approximate pressure of saturated vapour (p') at the temperature θ_1 (from REGNAULT's tables).

,, XIV. The difference between Cols. XIII. and XII. This indicates the limit of fall of pressure from the flask to the condenser, *i.e.*, along about 19 feet of narrow tubing. It must be remembered that owing to the presence of the H_2SO_4 the pressure in the condenser fell off greatly, and Col. XIII. is only useful as indicating a value considerably exceeding the real difference between p' and p''. No use is made of this quantity in the reduction of the observations.

TABLE XI. (*a*).—Experimental Results at Temperatures nearly 40° C. Number of Cells in Series* = 4.

I. Number and date.	II. θ_0.	III. $m_1 - m_2 = M$.	IV. t_e.	V. t_s.	VI. r_1.	VII. $\theta'_0 - \theta''_0$.	VIII. $d' - d''$.	IX. C_{θ_1}.	X. Temp. cells.	XI. R_1.	XII. p''.	XIII. p'.	XIV. $p' - p''$.
											millims.	millims.	millims.
I. Sept. 17 .	4$\overset{\circ}{0}$·147	3·7852	2866·4	3220·?	5·235	$\overset{\circ}{0}$	−·$\overset{\circ}{0}$276	318	15·12	10·379	46	55	9
II. " 18 .	40·146	3·7954	2851·8	4077·7	5·266	+·0005	+·0049	318	15·04	10·379	47	55	8
III. " 18 .	40·147	3·5039	2635·1	3811·2	5·420	−·0030	+·0037	318	15·18	10·379	47	55	8
IV. " 19 .	40·144	3·5240	2648·0	3732·1	5·252	−·0045	+·0102	318	14·96	10·379	46	55	9
V. " 19 .	40·145	2·5217	2650·3	3518·4	5·314	−·0055	+·0163	318	15·14	10·379	46	55	9
VI. " 20 .	40·147	3·8558	2899·5	4890·5	5·357	0	−·0108	318	15·04	10·379	47	55	8
VII. " 21 .	40·147	3·7677	2825·1	3714·0	5·515	−·0005	+·0108	318	14·99	10·379	46	55	9
VIII. " 21 .	40·147	3·8564	2902·0	3984·3	5·339	−·0040	+·0026	318	15·04	10·379	46	55	9
IX. " 22 .	40·149	4·0046	3007·9	4499·6	5·259	0	−·0002	318	14·92	10·379	47	55	8
X. " 23 .	40·157	4·0088	3005·1	4395·1	5·440	−·0090	+·0124	318	14·91	10·379	47	55	8
XI. " 26 .	40·133	4·0037	3006·0	4129·2	5·307	0	−·0006	318	13·86	10·379	47	55	8

* Number of cells actually in use = 16.

TABLE XII. (*a*).—Experimental Results at Temperatures near 30° C. Number of Cells in Series = 4.

I. Number and date.	II. θ_0.	III. $m_1 - m_2 = M$.	IV. t_e.	V. t_s.	VI. r_1.	VII. $\theta'_0 - \theta''_0$.	VIII. $d' - d''$.	IX. C_{θ_1}.	X. Temp. cells.	XI. R_1.	XII. p''.	XIII. p'.	XIV. $p'-p'$.
											millims.	millims.	millims.
XII. Oct. 4 .	29°·987	4·0017	3022·8	4515·7	5·314	0°	−°·0123	312	15·02	10·354	23	31	8
XIII. " 6 .	29·983	3·9894	3007·3	4364·1	5·411	−·0015	0	312	14·86	10·354	24	31	7
XIV. " 8 .	29·998	3·9872	3007·5	4532·5	5·386	0	−·0040	312	14·96	10·354	23	31	8
XV. " 9 .	29·999	3·9919	3010·3	4628·0	5·294	+·0010	+·0020	312	14·92	10·354	23	31	8
XVI. " 11 .	30·004	4·2015	3169·9	5003·7	5·195	−·0020	+·0031	312	14·96	10·354	24	31	7

TABLE XIII. (*a*).—Results near 30° C. Number of Cells in Series = 3.

I. Number and date.	II. θ_0.	III. $m_1 - m_2 = M$.	IV. t_e.	V. t_s.	VI. r_1.	VII. $\theta'_0 - \theta''_0$.	VIII. $d' - d''$.	IX. C_{θ_1}.	X. Temp. cells.	XI. R_1.	XII. p''.	XIII. p'.	XIV. $p'-p''$.
											millims.	millims.	millims.
XVII.* Oct. 12	29°·993	3·0870	4109·8	5691·0	5·257	−°·0010	+°·0006	312	14·96	10·352	25	31	6
XVIII. " 13	29·993	3·0910	4116·6	2969·3† 2294·4	5·313 5·423	−·0005	−·0049	312	14·92	10·352	26	31	5

* The potential difference at the ends of the coil was uncertain during the first minute or so of this experiment, owing to a false contact in the Clark cell circuit. After rectifying the mistake it was found that the previous approximate adjustment of the rheochord had made the D.P. slightly too low, and thus t_e is too long, but not by as much as a second, for the error in D.P. during this interval (which certainly did not amount to two minutes) was less than E/500, as shown by the movement given to the rheochord.

† The chronograph tape showed that for some unknown reason the stirring rate suddenly altered at about 3000 seconds from the start. Thus the stirring correction has to be applied in two portions.

Reduction of the Observations given in Tables XI. (*a*) to XIII. (*a*).

(See Tables XII. (*b*) to XIII. (*b*).)

Col. XV. gives the value of $Q_e t_e = \frac{(ne)^2 \times t_e}{R_1 \times J}$.

The correction for temperature of the cells was made by Lord RAYLEIGH'S coefficient (·00077), but, as an inspection of Col. X. (*supra*) will show, the correction was in every case very small, except in XI. During the night of September 25 the Clark cell tank regulator ceased to work, and I found the cells at a temperature of 13°·8 the next morning. I considered it better to keep them at that temperature throughout the day than to raise it to 15° a few hours before an experiment. The correction in this case amounts to 1 in 1500, but is probably accurate to 1 in 5000.

In a communication to the Royal Society, on November 22, 1894, Professor SCHUSTER pointed out an error in my determination of the value of J, viz., that I had not made a necessary correction for the specific heat of the air displaced by the water, for the method I adopted gave the difference in the rate of rise when a certain space was filled first with air and then with water. This correction raises my value of J by 1 in 4000. Hence, in the following reductions I assume $J = 4{\cdot}199$ in place of 4·198.* As I have before pointed out, if in consequence of errors in my standards, &c., my value of J is inaccurate, it is still the right value to insert *here*, where I use the same standards, for errors of the kind referred to are thus eliminated.

Col. XVI. The value of Q_s as deduced from Col. VI. by means of Table VI., Section VII. (*supra*).
,, XVII. The "stirring supply" $Q_s t_s$ from Cols. XVI. and V.
,, XVIII. The term $\Sigma q = C_{\theta_1} \{(\theta'_0 - \theta''_0) - (d' - d'')\}$ from Cols. VII., VIII., and IX.
,, XIX. Gives the sum of Cols. XV., XVII., and XVIII., that is, the total number of thermal grams used in evaporating the mass M (Col. III.).
,, XX. Repeats the value of θ_0, in order to render the reference less troublesome.
,, XXI. The value of L, deduced from the equation $L = \frac{Q_e t_e + Q_s t_s + \Sigma q}{M}$.

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* This correction should *not* be applied to the values of the specific heat of aniline given in Paper A. In that case the results also depended on the observations of *differences*, and if the corrected value of J was there used, a further correction for the specific heat of the air displaced by the aniline would have to be made, the final values remaining practically unaltered.

TABLE XI. (*b*).—Reduction of the Observations in Table XI. (*a*). ($n = 4$.)

Experiment.	XV. $Q_e t_e$.	XVI. Q_s.	XVII. $Q_s t_s$.	XVIII. Σq.	XIX. Σ.	XX. θ_0.	XXI. L.
I.	2164·0	·00443	14·3	−8·8	2169·5	40°·147	573·11
II.	2152·1	·00454	18·5	+1·7	2172·3	40·146	572·31
III.	1987·3	·00509	19·4	+0·2	2006·9	40·147	572·77
IV.	1999·5	·00449	16·8	+1·8	2018·1	40·144	572·61
V.	2000·9	·00471	16·6	+3·4	2020·9	40·145	573·80
VI.	2189·1	·00486	23·8	−3·4	2209·5	40·147	573·01
VII.	2133·4	·00546	20·3	+3·3	2157·0	40·147	572·50
VIII.	2191·0	·00480	19·1	−0·4	2209·7	40·147	573·00
IX.	2271·7	·00452	20·3	−0·1	2291·9	40·149	572·28
X.	2269·7	·00517	22·7	+1·1	2293·5	40·157	572·12
XI.	2273·6	·00468	19·3	−0·2	2292·7	40·133	572·61
Mean of all						40·146	572·74
Mean of Nos. VI. to XI. . . .						40·147	572·59

TABLE XII. (*b*).—Reduction of the Observations in Table XII. (*a*). ($n = 4$.)

Experiment.	XV. $Q_e t_e$.	XVI. Q_s.	XVII. $Q_s t_s$.	XVIII. Σq.	XIX. Σ.	XX. θ_0.	XXI. L.
XII.	2288·5	·00672	30·4	−3·8	2315·1	29°·987	578·58
XIII.	2277·2	·00723	31·6	−0·5	2308·3	29·983	578·64
XIV.	2276·9	·00710	32·1	−1·3	2307·7	29·998	578·78
XV.	2279·3	·00663	30·7	+0·9	2310·9	29·999	578·90
XVI.	2400·1	·00614	30·7	+0·2	2431·0	30·004	578·60
Mean						29·994	578·70

TABLE XIII. (*b*).—Reduction of the Observations in Table XIII. (*a*). ($n = 3$.)

Experiment.	XV. $Q_e t_e$.	XVI. Q_s.	XVII. $Q_s t_s$.	XVIII. Σq.	XIX. Σ.	XX. θ_0.	XXI. L.
XVII.	1750·1	·00644	36·7	−0·1	1786·7	29°·993	578·83
XVIII.	1753·4	·00696	36·7	−1·7	1788·4	29·993	578·60
Mean						29·993	578·72

I have already remarked that I attach more value to Experiments VI. to XI. than to the preceding ones, and I shall therefore assume the mean value of L at 40°·15 as 572·60.

The close agreement between the means of Nos. XII. to XVI. and Nos. XVII. and XVIII. is very satisfactory when it is remembered that the rate of evaporation is in the last case nearly halved.

I need scarcely say that, had time permitted, I should have performed more experiments, especially at 30°. I do not, however, consider that the evidence would have been greatly strengthened.

In the whole of the series from VI. onwards (*i.e.*, after the adoption of the bent form of dropper) there is no experiment which gives results differing from the mean at that temperature by more than 1 in 1430, and in the groups at 30° the greatest divergence is 1 in 2900. The probable mean error of a small group of experimental results of this kind is therefore less than the probable error of some of the constants on which our conclusions are based, and a larger accumulation of such experimental numbers would not necessarily bring us any nearer to the absolute value.

Conclusions.

Temperature. Nitrogen thermometer.	Value of L (in terms of thermal unit at 15° C.).
40°·15 C.	**572·60**
30°·00 C.	**578·70**

Section XI.—Discussion of the Results.

From the conclusions arrived at in the last section we obtain (over the range 30° to 40°·15 C.) $dL/d\theta = \cdot 6010$.

Suppose we assume with Regnault that L is a linear function of θ, it follows that

$$\text{when } \theta = 0^\circ, \quad L = 596\cdot 73$$
$$,, \quad \theta = 100^\circ, \ L = 536\cdot 63$$

I admit the folly of attempting to extrapolate to such an extent where we have no evidence but that given by the experiments themselves. It is a different matter when we can bring forward independent evidence.

In Section II. I dwelt upon the importance of the experiments of Dieterici at low, and of Regnault at high temperatures; the agreement between the values obtained by those observers and the ones resulting from the above extrapolation is so extraordinary that I give in detail their experimental numbers.

As stated in Table I., *ante*, the mean value of all Dieterici's experiments was 596·8 at 0°. He, however, regards certain of the experiments (whose results are given in his Tables II. and IV.) as of greater value than others, because the evaporating water was included in a platinum instead of a glass tube, and thus its temperature must have approximated more nearly to the external temperature. His numbers are as follows (‘Wied. Ann.,’ vol. 37, 1889, pp. 502–4) :—

TABLE XIV.—DIETERICI'S Experiments.

Table II.	597·29
	597·19
	595·99
	596·99
	596·76
	595·74
	596·51
	597·06
Table IV.	597·07 (with lower pressure)
	596·68
Mean of all experiments in platinum tubes	596·73

His own summary of these results is as follows :—

“Die Versuche mit dem Platingefässe ergeben

$$r = 596{\cdot}73$$

mit einem wahrscheinlichen Fehler des Mittels von ± 0·13.”*

REGNAULT performed forty-four experiments at temperatures about 100°. Of these he rejects Nos. 1 to 6, as merely preliminary ; the remainder are as follows. It should be remembered that the numbers in this table give the values of the “total heat,” not those of L.

TABLE XV.—REGNAULT'S Experiments.

Experiment.	Temperature.	“Total heat.”	Experiment.	Temperature.	“Total heat.”
	°			°	
7	99·49	636·8	26	100·22	637·2
8	99·46	636·3	27	100·37	636·1
9	99·31	636·4	28	100·32	636·1
10	99·28	637·6	29	100·32	637·3
11	100·19	636·0	30	100·31	636·1
12	100·19	636·8	31	100·22	635·6
13	100·19	638·3	32	100·22	636·9
14	100·19	637·9	33	100·26	635·9
15	100·19	635·9	34	100·26	635·9
16	100·26	635·9	35	99·09	635·7
17	100·26	637·9	36	99·09	636·1
18	100·26	637·9	37	99·07	636·6
19	100·26	635·6	38	99·07	636·9
20	100·26	635·8	39	99·36	636·1
21	100·26	636·7	40	99·36	636·8
22	100·22	637·6	41	99·33	637·3
23	100·22	638·4	42	99·33	636·4
24	100·22	636·8	43	99·27	635·7
25	100·22	636·6	44	99·27	636·8
			Mean . .	99·88	636·67

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* ‘Wied. Ann.,’ vol. 37, 1889, p. 504.

This value of 636·67 at 99°·88 would become 636·60 at 100°. If we assume that 1 gram of water gives out 100 thermal units in cooling from 100° to 0°, we get

$$L = 536{\cdot}60 \text{ at } 100°.$$

VALUES of L.

	0°.	100°.
REGNAULT	..	536·60
DIETERICI	596·73	..
GRIFFITHS (extrapolated) . .	596·73	536·63

I have learned to regard experimental coincidences with suspicion, they are so often misleading, but such an unusual case as the above merits attention.

These coincidences are the more extraordinary on account of the following considerations.

DIETERICI assumed (*ante*, p. 265) as his thermal unit the "mean thermal unit" from 0° to 100° C. Now according to REGNAULT* the ratio of the "mean thermal unit" to the thermal unit at 0° is as 1·005 to 1.

If we assume ROWLAND'S or BARTOLI and STRACCIATI'S determinations of the changes below 15° (my own have not extended below that temperature) we should get

$$\frac{\text{“mean thermal unit”}}{\text{“thermal unit at } 15°\text{”}} = \frac{1{\cdot}005}{{\cdot}994} \text{ approximately,}$$

i.e., $\frac{1{\cdot}011}{1}$ and thus DIETERICI'S value of L, if expressed in terms of the same thermal unit as I have used, would be increased to 603·3.

Again, according to REGNAULT we ought to subtract 100·5 from 636·60 in order to obtain the value of L at 100. This would give L = 536·1.

Some further considerations, however, tend to show that the agreement at both ends of the line given by my observations is not merely fortuitous. We can deduce the values of L resulting from my "exhaust" experiments (at any temperature θ) by the formula,

$$L = 596{\cdot}73 - {\cdot}6010\,\theta \quad . \; . \; . \quad (G_1).$$

Now the preliminary experiments (see Table IX., *ante*) although irregular, carry some weight and the mean of each group is in fair agreement with formula (G_1).

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* "De la Chaleur Spécifique," 'Mémoires de l'Académie des Sciences,' tome 21.

TABLE XVI.

Temperature.	L from "preliminary" observations (Table IX.)	L from formula G_1.
25°·0	581·9	581·70
40·0	572·4	572·69
49·8	566·5	566·80

I have given in Section II. my reasons for rejecting REGNAULT'S experiments at low temperatures, where he determined the temperature in the calorimeter from the pressure of the vapour in the condenser. The objections there brought forward, however, lost all force as regards these experiments above 63° in which the methods of observation and experiment were altered.

Column III. of the following table gives the results of all REGNAULT'S experiments above 63° and below 100° . . . (R_e), Column IV. gives the values resulting from REGNAULT'S own formula $606{\cdot}5 + {\cdot}305t$ . . . . (R), Column V. contains those given by WINKELMANN'S formula* . . (W), which includes REGNAULT'S expression for the capacity for heat of water, and Column VI. the numbers obtained by assuming the validity of formula G_1 (*supra*), from which we deduce

$$\text{Total Heat} = 596{\cdot}73 + {\cdot}3990\theta \;.\;.\;.\;.\; (G_2).$$

Column VII. gives the difference between (R_e) and (R), in Column VIII. are given the differences between (R_e) and (W), and Column IX. shows the differences between (R_e) and (G_2).

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* $L = 589{\cdot}5 - 0{\cdot}2972t - 0{\cdot}0032147t^2 + 0{\cdot}000008147t^3$.

TABLE XVII.—Comparison between REGNAULT'S Experimental Results (R_e) over the Range 63° to 88°, with the value given by formulæ (R), (W), and (G_2).

I. No. of experiment.	II. Temperature.	III. Experimental results. (R_e.)	IV. (R.)	V. (W.)	VI. (G_2.)	VII. (R_e)−(R).	VIII. (R_e)−(W).	IX. (R_e)−(G_2).
1	88·11°	633·4	633·4	632·4	631·9	0	+ 0·9	+1·5
2	87·83	633·1	633·2	632·3	631·8	− 0·1	+ 0·8	+1·3
3	85·97	628·4	632·7	631·7	631·0	− 4·3	− 3·3	−2·6
4	85·24	628·6	632·5	631·5	630·7	− 3·9	− 2·9	−2·1
5	85·20	631·7	632·5	631·5	630·7	− 0·8	+ 0·2	+1·0
6	84·68	629·9	632·3	631·2	630·5	− 2·4	− 1·3	−0·6
7	83·08	628·9	631·8	630·7	629·9	− 2·9	− 1·8	−1·0
8	82·66	631·0	631·7	630·6	629·7	− 0·7	+ 0·4	+1·3
9	81·03	628·8	631·2	630·0	629·1	− 2·4	− 1·2	−0·3
10	80·60	627·7	631·1	629·9	628·9	− 3·4	− 2·2	−1·2
11	80·37	628·8	631·0	629·8	628·8	− 2·2	− 1·0	0
12	80·17	630·2	630·9	629·7	628·7	− 0·7	+ 0·5	+1·5
13	79·55	630·1	630·8	629·5	628·5	− 0·7	+ 0·7	+1·6
14	78·28	627·0	630·3	629·0	628·0	− 3·3	− 2·0	−1·0
15	76·50	628·6	629·8	628·3	627·2	− 1·2	+ 0·3	+1·4
16	71·35	624·4	628·2	626·4	625·2	− 3·8	− 2·0	−0·8
17	71·11	622·2	628·1	626·3	625·1	− 5·9	− 4·1	−2·9
18	70·49	626·9	628·0	626·1	624·9	− 1·1	+ 0·8	+2·0
19	69·70	626·4	627·7	625·7	624·5	− 1·3	+ 0·7	+1·9
20	68·01	622·5	627·3	625·1	623·9	− 4·8	− 2·6	−1·4
21	66·30	624·7	626·7	624·5	623·2	− 2·0	+ 0·2	+1·5
22	64·34	622·9	626·1	623·9	622·4	− 3·2	− 1·0	+0·5
23	63·02	625·5	625·7	623·2	621·9	− 0·2	+ 2·3	+3·6
Sum of differences						−49·3	−17·6	+5·2
Mean difference						− 2·14	− 0·77	+0·23
If we omit Experiment 23, we get Sum of differences						−49·1	−19·9	+1·6
Mean difference						− 2·23	− 0·90	+0·07

The results of the above comparison show that over the range 63° to 88° the formula (G_2) gives a closer approximation to REGNAULT'S experimental numbers than either of the other formulæ.

The only reasonable explanation of these various coincidences which occurs to me is that the value of the "mean thermal unit" is practically the same as the value of the "thermal unit at 15° C."*

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* Further evidence can be adduced in support of this view. In Section II. I pointed out that if we express the results of the observations of BUNSEN and REGNAULT, on the latent heat of fusion of

I see nothing impossible in this supposition. As stated in Section II. there is sufficient evidence that at low temperatures the capacity for heat decreases with rise of temperature. ROWLAND found a minimum indicated near 34°. If therefore the capacity for heat increases gradually above some such temperature, but more rapidly near 100°, it is quite conceivable that the "mean thermal unit" should closely approximate to the "thermal unit at 15° C." Our only experimental evidence to the contrary is that given by REGNAULT in his paper, "De la Chaleur Spécifique." We know that his conclusions at low temperatures are incorrect, and I do not see that those at higher temperatures have greater value, for his methods of observation and experiment were, in this case, unaltered.

The matter, of course, can only be cleared up by a direct determination of the capacity for heat of water over the range 0° to 100°.

In the meantime I contend that the evidence in favour of the formula "total heat $= 596{\cdot}73 + {\cdot}3990\,\theta$" is stronger than that upon which either REGNAULT'S or WINKELMANN'S formulæ are based.

At temperatures above 100° the values of "the total heat" deduced by formula (G_2) would be higher than REGNAULT'S experimental numbers. The capacity for heat of water at higher temperatures is so uncertain, and it has so great an influence on the values of L at high temperatures when deduced from the "total heat" formulæ, that I do not feel that a discussion on these results would at present be of any value.

The results of the experimental work described in preceding sections, and of the evidence brought forward in this section, may be summarised as follows :—

THE VALUES OBTAINED BY DIETERICI AT 0°, BY REGNAULT AT TEMPERATURES 63° TO 100° C., AND BY GRIFFITHS AT INTERMEDIATE TEMPERATURES ARE (ASSUMING THE APPROXIMATE EQUALITY OF THE "MEAN THERMAL UNIT" AND THE THERMAL UNIT AT 15° C.) CLOSELY REPRESENTED BY THE FORMULA

$$\mathbf{L = 596{\cdot}73 - 0{\cdot}6010\theta.}$$

[Note, May 7, 1895.—The suggestion that the "mean thermal unit" does not exceed the "thermal unit at 15° C." has been criticized as over bold. It is, therefore, with peculiar pleasure that I include in this paper a communication which I have to-day received from Dr. JOLY, to whom I return my sincere thanks for his permission to publish it.

Dr. JOLY informs me that he regards his experiments as preliminary; their importance, however, is undoubtedly great. They are (I believe) the first experiments since those of REGNAULT which throw any light on the relative values of the two units. It will be seen that (assuming BARTOLI and STRACCIATI'S conclusions as to the changes in the capacity for heat of water from 0° to 15° C.) the results of Dr. JOLY'S experiments indicate that the ratio

ice in terms of the same unit, by means of the ordinarily accepted comparison of the values of their respective thermal units, their difference becomes excessive.

$$\frac{\text{Mean thermal unit}}{\text{Thermal unit at } 15^\circ \text{ C.}} = \frac{9952}{9995} = \frac{0{\cdot}9957}{1}$$

in place of $\frac{1{\cdot}011}{1}$.

It is apparent that there is sufficient evidence to justify scepticism as to the validity of the commonly accepted ratio, and I hope that the demonstration of this uncertainty may quicken further investigation into the actual value of this important constant.

Note (*by Dr.* J. JOLY, *F.R.S.*) *on the Ratio of the Latent Heat of Steam to the Specific Heat of Water.*

Upon receiving from Mr. GRIFFITHS a copy of the abstract of his paper on the latent heat of steam, I determined upon making some experiments with the steam calorimeter on the ratio of the latent heat of steam to the mean specific heat of water over the range air temperature 12° to 100°. Pending the completion of a form of the calorimeter which will enable me to make this comparison over suitable and definite ranges of temperature, I gladly add, at Mr. GRIFFITHS' request, the following note on the experiments already made.

The weight of water operated upon was 12·8545 grms. This was enclosed in a thin blown glass bulb, sealed while the water was boiling, and having an internal volume of 15·714 cub. centims. Ten experiments were made—these were in close agreement. The mean initial temperature was 11°·89; the mean steam temperature 99°·96. The first temperature was determined by a Kew-corrected thermometer reading tenths on an open scale; the second temperature determined by a standard barometer. The mean weight of steam condensed was 2·32917 grms.

To correct this for the effect of the glass vessel, six experiments were made on the latter when containing dry air only. Further corrections were made (*a*) for evaporation within the vessel when containing water; (*b*) for buoyancy or displacement effect on the apparent weight of the vessel, the densities being not quite the same in the experiments on the filled and empty vessel; (*c*) for the specific heat of the air contained in the vessel when empty of water. A total subtractive correction of 0·2298 grm. was obtained.

If we now calculate the mean specific heat of water between 11°·89 and 99°·96, assuming the value of the latent heat of steam given by Mr. GRIFFITHS' formula, *i.e.*, $L = 596{\cdot}73 - {\cdot}6010\,\theta$, where θ has the value 99°·96, we get

$$C = \frac{2{\cdot}0994 \times 536{\cdot}66}{12{\cdot}8545 \times 88{\cdot}07} = 0{\cdot}99520.$$

I have little doubt that this will remain—closely—the mean specific heat, 12°–100°, according to the steam calorimeter. It will, of course, be necessary to check the result by further experiments. It is true I formerly made experiments in the steam calorimeter and obtained a higher value, but it was in an early and very defective form of the instrument, and an error of positive sign, as I afterwards found, very certainly obtained in those experiments.

Considering this number in the light of Mr. GRIFFITHS' remarks, it certainly supports his contention that REGNAULT made an error of excess in his value of the mean calorie—0° to 100°. The above number is however, even less than the value supposed by Mr. GRIFFITHS to be the true number. For, as I understand, Mr. GRIFFITHS' L is calculated on the calorie at 15° C. as unity. If this is also —as Mr. GRIFFITHS suggests as probable—in close agreement with the mean calorie, 0° to 100°, then the mean specific heat from 12 to 100 should come out only a very little less than unity. In fact, by plotting BARTOLI and STRACCIATI'S observations below 15°, we can estimate what the mean specific heat from 12° to 100° ought to be if the mean from 0 to 100 is the same as the specific heat at 15° and both equal unity. A rough estimate gives this to be 0·9995.

My value is therefore too low to be in harmony with the supposition that the mean calorie and the 15° unit are *identical.* The value of the latent heat of steam is, of course, involved, for the steam calorimeter can only give a ratio, and, if the number now obtained is correct, it follows that either the latent heat assumed is too low, or the specific heat of water is even lower than it is supposed to be, or possibly both are somewhat incorrect.

J. JOLY.

Physical Laboratory,
Trinity College, Dublin.]

Section XII.—THE DENSITY AND SPECIFIC VOLUME OF SATURATED WATER-VAPOUR DEDUCED BY MEANS OF THE THERMODYNAMIC EQUATION FROM THE VALUES OF L GIVEN BY FORMULA (G_1).

WINKELMANN (as previously stated) assigns to what he terms the "theoretical density" of water-vapour the value 0·6225 (air = 1). He gives, however, no information regarding the data for this statement.

The most recent investigation of the comparative volumes in which oxygen and hydrogen combine is that by SCOTT, whose conclusions are as follows:* "That 100,000 volumes of oxygen unite with 200,245 volumes of hydrogen to form water. Applying this to the density of oxygen found by Lord RAYLEIGH to be 15·882, we get for the atomic weight of oxygen 15·862."

In close agreement with this conclusion we have—

DITTMAR	15·866
COOKE and RICHARDS	15·869

---

* 'Phil. Trans.,' A, 1893, p. 567. Also 'Science Progress,' August, 1894.

Assuming SCOTT and RAYLEIGH'S values we get—

Molecular weight of water-vapour = 17·862.

Lord RAYLEIGH in 1888–9* pointed out that REGNAULT'S conclusions as to the weights of unit volumes of hydrogen and air required correction, as REGNAULT had not allowed for the change in volume of the bulb consequent on changes in pressure. CRAFTS† has applied this correction, and finds the resulting comparative densities of air and hydrogen to be as follows :—

	REGNAULT'S value.	Corrected value.
Air	1	1
Hydrogen	·06927	·06949 (p. 1664, *ibid.*)

OSTWALD‡ deduces from these numbers the weights of 1 litre at 0° and 76 centims., as

Air, 1·29349 grams. Hydrogen, ·08988 gram.

Hence we get

"Theoretical Density" of water-vapour = **·6206** (air = 1).

I will now proceed to deduce the density at various temperatures by means of the thermodynamic equation

$$L = \frac{T}{J}(s' - s)\frac{dp}{dT},$$

and I assume the values of the various quantities to be as follows :—

$J = 4·199 \times 10^7$. (My value after SCHUSTER'S correction for the specific heat of the displaced air, see p. 314, *supra*).

$L = 596·73 - ·6010\,\theta$ . . . formula G_1 (*supra*).

$T = 273·7 + \theta$.

The values of dp/dT are taken from BROCH'S reduction of REGNAULT'S experimental results,§ and are as follows :—

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[*] 'Proc. Roy. Soc.,' vols. 43 and 45.

[†] 'Comptes Rendus,' vol. 106, pp. 1662–4, 1888.

[‡] 2nd ed., vol. 1, p. 181.

[§] 'Trav. et Mém. du Bur. Intern. des Poids et Mes.,' 1, A, 1881.

TABLE XVIII.

I. θ.	II. $\frac{dp}{dT}$ (millim. of Hg).	III. $\frac{dp}{dT}$ (dynes per sq. centim.).	IV. p (millim. of Hg).
° 0	·330	4401·1	4·569
20	1·073	14308	17·363
40	2·936	39150	54·865
60	6·922	92301	148·89
80	14·388	191850	354·87
100	26·981	359800	760·

The numbers in Column III. are obtained by assuming $g = 980·94$ and density of mercury $= 13·596$.

The resulting values of s' (specific volume) and d (density, air $= 1$) are given in the following table :—

TABLE XIX.

I. Temperature.	II. s'.	III. Specific volume of air.	IV. d.
° 0	207970	128600	·6184
20	58430	36318	·6215
40	19581	12278	·6270
60	7644	4814	·6298
80	3395·6	2141	·6305
100	1676·9	1056·2	·6299

The specific volume of air was calculated by the formula

$$\frac{1}{·0012935} \times \frac{(273·0 + \theta)}{273·0} \times \frac{760}{p} = 2152·2 \times \frac{273·0 + \theta}{p}.$$

The value of $dp/d\mathrm{T}$ at low temperatures is not known with sufficient precision to enable us to attach any weight to the resulting values of d. For example, if we take $dp/d\mathrm{T} = ·331$ millim. at 0° instead of ·330 millim., we get $d = ·6204$ in place of ·6184. At temperatures above 20° or 30°, not only is the value of $dp/d\mathrm{T}$ known with greater certainty, but the effect of any small error is diminished.

A comparison of the "Theoretical Density" (·6206) with the numbers in Column IV. of the last table, indicates that aqueous vapour at low pressures approximates in density to that of a perfect gas, but that, at higher pressures, its density exceeds that of a perfect gas.

Above a pressure of about 140 millims., it appears to attain a practically constant density about 1·015 times that of the "theoretical" one.

I have previously pointed out that the values of L given by my experiments are independent of errors in the electrical standards used during my determination of J. This, however, is not the case when the density is obtained from the thermo-dynamic equation, as the results then depend upon the absolute value assigned to the mechanical equivalent. Now my corrected value of J exceeds Professor Schuster and Mr. Gannon's by about 1 in 1000, hence the values of *d* in Col. IV., Table XIX., would, according to Schuster, have to be increased by ·0006, whereas if we use Rowland's value (4·190) the increase would be about ·0012.

I have given the above determination of the relative densities of water-vapour and air, because it was the method of calculation adopted by Winkelmann, and therefore enables a comparison to be made between his conclusions and those arrived at by the use of formula G_1 (*supra*). It appears to me to be an unsatisfactory method, as it involves unnecessary data regarding air. A more direct way of obtaining some information concerning the density of water-vapour, is that of finding PV, *i.e.*, the "volume energy." Now $PV = RT$, and the value of R for a true gas is 0·0815,* when P is pressure in atmospheres, and V the volume in litres occupied by the molecular weight in grams. Assuming as before the molecular weight of water to be 17·862, and obtaining the values of V and P from Col. II., Table XIX., and Col. IV., Table XVIII., we get:—

Temperature.	$\frac{PV}{T} = R.$	
0°	·0827	as compared with ·0826 in the case of hydrogen.
20	·0823	
40	·0816	
60	·0812	
80	·0811	
100	·0812	

and here again we find that at temperatures near 0° water-vapour resembles a true gas.

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* This value of R depends on the assumptions that 1 litre of hydrogen at 0° and 76 centims. weighs 0·08988 gram. (*supra*), and that the coefficient of expansion of hydrogen = ·0036613 (the value obtained by Callendar and myself in 1893). Dr. Shields, however, assigns to R the value 0·0819 (see 'Science Progress,' December, 1894).

Appendix I.—DETAILS OF STIRRING EXPERIMENTS WHEN THE CALORIMETER WAS FILLED WITH OIL.

The tank temperature having become steady (at θ_0), the calorimeter was raised to a temperature θ_1, slightly below θ_0. In order that the conditions should become steady, the stirring was allowed to proceed for half-an-hour to one hour, before observations were commenced. The battery key (k_5, Plate 6, fig. 2) was kept continually oscillating and, as the temperature rose, the swings of the galvanometer diminished, until no motion was observed on reversing the battery circuit. The observer then pressed a key communicating with the chronograph, and thus the time was recorded. As before stated, the stirrer automatically registered its own revolutions. At the same moment that the observer at the galvanometer pressed his recording key,* a second observer took the readings on the mercury thermometer, which gave the temperature of the steel walls.

As any change in the mercury thermometer was of great importance, this observation was made with the micrometer eye-piece before referred to.

Groups of five observations were taken about certain previously fixed bridge-wire readings, and each group of five was meaned to find the time of passing the given points.

The following Table gives full particulars of a stirring experiment. It is by no means a good one, but I give it simply because it is the first one done after the introduction of the oil. The exterior temperature was unusually unsteady.

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* In the slower experiments, however, instead of using the chronograph, I called the transit, and my assistant recorded the time, as also the time of the revolutions, the stirrer ringing a bell at each 1000.

TABLE XX.—Stirring experiment No. I., September 17. Temperature of bridge-wire = 64°·2 F.

Bridge-wire reading.	Time of transit.	Reading thermometer II.	No. of revolutions.	Time of revolutions.
	P.M.	millims.		
589·8	9 45 16	882·40	0	9 47 36
590·2	9 48 48	882·40		
590·6	9 52 58	882·42		
591·0	9 56 58	882·42		
591·4	9 59 49	882·40	4000	10 0 12
Means . 590·6	9 52 46	882·41		
594·2	10 20 11	882·41	9000	10 15 55
594·6	10 24 39	882·40		
595·0	10 28 34	882·41		
595·4	10 32 20	882·48	14000	10 31 39
595·8	10 36 36	882·45		
Means . 595·0	10 28 40	882·43		
598·7	11 3 30	882·46		
599·1	11 6 58	882·42		
599·5	11 11 0	882·40	27000	11 12 30
599·9	11 14 4	882·40		
600·3	11 18 30	882·40		
Means . 599·5	11 10 48	882·42		
602·9	11 48 28	882·38	39000	11 50 15
603·3	11 51 52	882·38		
603·7	11 56 54	882·38		
604·1	12 1 44	882·39	42000	11 59 42
604·5	12 6 12	882·40	45000	12 9 9
Means . 603·7	11 57 2	882·39	Mean time per 1000 = 188·73 Hence, rate per 1 sec. = 5·299	

882·41, No. II., = 40°·143 C., and 1 millim. of No. II. at 882 = ·0501° C.

1 millim. of bridge-wire (temperature 15°) at 40°·1 = ·009101° C., therefore, 1 millim. of No. II. = 5·51 millims. of bridge-wire.

The times of transit may appear, and no doubt are, very irregular. It must be remembered, however, that the rise in temperature between the individual observations in each group was not so much as 0°·004 C. As this rise took about four minutes, it is evident that the time of transit of so slow a movement cannot be accurately determined, but observational errors of this kind are precisely those where a close approximation is secured by taking the mean of a group. If the middle observation of each group is compared with the mean, it is evident that an individual observation might be in error by as much as 20 seconds (the greatest difference in the above table is 12 seconds), but it is improbable that the mean is in error by more than 5 seconds. The example given is the one which had the slowest rate of rise, and hence the discrepancies are more marked than would otherwise be the case. As the total time of the experiment was about 2 hours 20 minutes, an error of even 10 seconds in the mean of each group would affect the result by but 1 in 800, and as an error of 1 in 50 in the value of Q_s would only affect my final values of L by 1 in 5000, the above order of accuracy was more than sufficient.

I will now give the reduction of the observation in the above table.

REDUCTION of Stirring Experiment No. I.

Bridge-wire range.	Time (t'').	Change in thermometer II.	Resulting change in range.	$\frac{d\theta_1}{dt}$.	Correction to mean bridge-wire.	Correction for temperature bridge-wire.	$\frac{d\theta_1}{dt}$ corrected.	
590·6–595·0	2154	+·02	+·11	·002094	−0·4	+1·7	·002090	A
595·0–599·5	2528	−·014	−·07	·001753	−1·2	+1·5	·001753	B
599·5–603·7	2772	−·030	−·17	·001454	+4·3	+1·2	·001460	C

Since A, B, and C should, if the exterior temperature (No. II.) had not changed, fall on a straight line, the most probable path is obtained by taking $\frac{1}{3}(2A + B)$ and $\frac{1}{3}(B + 2C)$ as the rate of rise at the corresponding bridge-wire readings, hence we get

Bridge-wire.	$d\theta_1/dt$.
594·28	·001978
600·15	·001558

Now the bridge-wire null-point $= 598·35 + ·03\theta_1$ (see p. 288). Therefore null-point at 40° $= 599·55$. We can now deduce the value of $d\theta_1/dt$ at this null-point. We get ·001600.

Hence

$$(d\theta_1/dt)_s = ·001600,$$

when $r_1 = 5·299$ and θ_1 is measured in millims. of the bridge-wire scale.

I think that there is no necessity to give details of the remaining experiments;

the following table shows the results of all those experiments at different rates where $\theta_0 = 40^\circ{\cdot}1$ approximately.

TABLE XXI.

Experiment.	Date.	$\left(\frac{d\theta_1}{dt}\right)_s$.	r.	Let t = time of rising 1 millim. of bridge-wire, then				
				tr $\times 10^{-1}$.	tr^2 $\times 10^{-2}$.	tr^3 $\times 10^{-2}$.	tr^4 $\times 10^{-3}$.	From formula A. (*infra*).
I.	Sept. 17	·001600	5·299	331	176	930	492	·001606
IX.	Oct. 27	·001626	5·310	327	173	921	489	·001619
VI.	„ 7	·001793	5·456	304	166	906	494	·001805
II.	Sept. 23	·002152	5·670	263	149	847	480	·002104
III.	„ 24	·008152	7·899	97	76	605	478	·007930

Experiments II. and III. were only performed with the object of ascertaining the effect of changes of rate. Although the differences between tr^4 may appear considerable, it must be remembered that this constant was only required in order to reduce experiments at different rates to some standard rate; in reality, when we consider that we are dealing with the fourth power of r the uniformity is remarkable.

If we plot the values of $(d\theta_1/dt)_s$ obtained from the formula

$$\left(\frac{d\theta_1}{dt}\right)_s = \frac{r^4}{491000} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(A)},$$

the results are in close agreement with the experimental ones, especially when the rate is between 5·2 and 5·5 (the extreme limits of rate during the Latent Heat experiments, the usual value being about 5·3). True, if we assume $(d\theta_1/dt)_s = r^3/92000$ our results would be nearly as close over the above limited range, but Experiments II. and III. indicate that the true relation is more nearly given by the previous expression. In any case, the difference between the experiments and the results as deduced from (A) do not differ by 1 in 100 over the above range of rate, and a difference of 1 in 100 in Q_s would only cause a difference of about 1 in 10,000 in L.

TABLE XXII.—The experiments at 30° give the following results.

Experiment.	Date.	$\left(\frac{d\theta_1}{dt}\right)_s$.	r.	$tr^3 \times 10^{-2}$.	$tr^4 \times 10^{-3}$.	From formula B (*infra*).
IV.	Sept. 29	·002330	5·280	629	333	·002314
VIII.	Oct. 27	·002380	5·320	632	337	·002383
VII.	„ 7	·002568	5·416	619	335	·002560
V.	„ 7	·005973	6·750	515	348	·006178

If we assume

$$tr^4 = 336000,$$

we get

$$\left(\frac{d\theta_1}{dt}\right)_s = \frac{r^4}{336000} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B).$$

And here again the differences between the experiments and the results from (B) are much below 1 per cent. at rates between 5·2 and 5·5, and again the experiment at higher speeds (Expt. V.) indicates that tr^4 is more constant than tr^3.

Applying formulæ (A) and (B), we can deduce the rise for a rate of 5·300.

Values of $(d\theta_1/dt)_s$ at rate 5·300 :—

Temperature.	$(d\theta_1/dt)_s$.
40°·1	·001608
30·0	·002348

Now (see Appendix II., Experiment IV.) it was found that when a similar experiment was performed at 40°·1, where the heat supply was that due to a potential difference of three Clark cells at 15° together with a stirring supply (at rate 5·277), then

$$(d\theta_1/dt)_{es} = \cdot 14853 \text{ (mean bridge-wire millim.).}$$

Now (from A) we get

$$(d\theta_1/dt)_s = \cdot 00158 \text{ at rate } 5\cdot 277, \quad \text{therefore } (d\theta_1/dt)_{3e} = \cdot 14695,$$

therefore

$$(d\theta_1/dt)_e = \frac{\cdot 14695}{9} = \cdot 01633,$$

hence

$$\frac{(d\theta_1/dt)_s}{(d\theta_1/dt)_e} = \frac{161}{1633} \text{ at rate } 5\cdot 300 \ (\textit{supra}) = \cdot 0986.$$

Now the corrected resistance at this temperature (Table VIII.) was 10·376 ohms where the D.P. was that of one Clark cell, and since

$$\mathrm{H} = \frac{e^2}{\mathrm{R}_1 \times \mathrm{J}} \text{ per sec.,} \quad \text{we have } \frac{1\cdot 4342^2}{10\cdot 376 \times 4\cdot 198} = \cdot 04723 \text{ thermal gram,}$$

therefore

$$\mathrm{Q}_s \text{ (rate } 5\cdot 300) = \cdot 04723 \times \cdot 0986 = \cdot 004659 \text{ thermal gram.}$$

In the same manner (Appendix II., Experiments V. and VI.) it was found that at temperature 30°

$$(d\theta_1/dt)_{3e} = \cdot15035, \quad \text{and } (d\theta_1/dt)_s = \cdot002348 \text{ (formula B, \textit{supra})},$$

hence

$$\frac{(d\theta_1/dt)_s}{(d\theta_1/dt)_e} = \frac{234\cdot8}{1671} = \cdot1405,$$

and at 30°

$$R_1 = 10\cdot348,$$

therefore

$$H = \frac{1\cdot4342^2}{10\cdot348 \times 4\cdot198} = \cdot04735 \text{ thermal gram per sec.}$$

therefore

$$Q_s \text{ (rate } 5\cdot300) = \cdot04735 \times \cdot1405 = \cdot006654 \text{ thermal gram.}$$

Now assuming (A) and (B), it follows that r^4/Q_s is constant, and we can deduce that if r_1 be any rate and 5·300 the standard rate

$$\text{At temp. } 40^\circ{\cdot}1,\ Q_s = \cdot004659 + (r_1^4 - 789) \times \cdot0000059 \quad . \quad . \quad . \quad . \quad (C).$$
$$\text{At temp. } 30^\circ{\cdot}0,\ Q_s = \cdot006654 + (r_1^4 - 789) \times \cdot0000084 \quad . \quad . \quad . \quad . \quad (D).$$

I performed one stirring experiment at 50° and two at 20° and I give the results only, as the values of Q_s at these temperatures are not required for the reduction of the L experiments described in this paper. I was unable (for want of time) to prove how nearly the effect of changes of rate could be expressed in the same manner as at 30° and 40°, but as the rate was nearly 5·3, the corrections introduced by the reduction to rate 5·3 were very small. The results were of use, as on plotting the curve for the values of Q_s at the four different temperatures it showed no signs of irregularity, and thus gave additional strength to the determinations at 30° and 40°. The values are as follows:—

$$\text{At temp. } 50^\circ,\ Q_s = \cdot00235 + (r_1^4 - 789) \times \cdot0000030 \quad . \quad . \quad . \quad . \quad (E).$$
$$\text{At temp. } 20^\circ,\ Q_s = \cdot00768 + (r_1^4 - 789) \times \cdot0000098 \quad . \quad . \quad . \quad . \quad (F).$$

The values of Q_s at 30° and 40° receive a certain amount of support from the preliminary experiments referred to in Section VII. Although my results by that method varied considerably amongst themselves, the mean of five experiments at 40° gave ·00000802 gram of water evaporated per 1 sec. by the stirring after reduction to rate 5·3, and the mean of four experiments at 30° gave ·00001137 gram of H_2O evaporated per sec. at the same rate.

Now, if we assume L at 40° = 573 and L at 30° = 579, we can deduce the values of Q_s, which are as follows :—

$$\text{At } 40°, Q_s = \cdot 00460$$
$$\text{,, } 30°, Q_s = \cdot 00658.$$

These results differ from those obtained without any weighing or passing of air (equations C and D *supra*) by 1 in 77 and 1 in 94 respectively. As an order of accuracy of 1 in 50 was sufficient for my purpose, I considered this independent evidence valuable, although I believe the former method to be by far the most exact.

I also performed a determination of Q_s at 50° by an evaporating experiment. This gave ·00000521 gram per sec. Assuming $L = 567$, this would give $Q_s = \cdot 00295$, far too high a value as compared with that given by equation (E). This evaporation experiment was a very unsatisfactory one, however, and I attach but little importance to it—in any case, the doubt would not affect the values of L.

To conclude this portion of the subject, I admit that it would have been advisable to perform more of these stirring experiments at 30° and 40°, but at the same time, I think the evidence is sufficient to warrant the assumption that the values of Q_s cannot be in error by as much as 1 in 50 and are probably correct to better than 1 in 100.

Appendix II.—DETAILS OF THE EXPERIMENTS BY WHICH THE CAPACITY FOR HEAT OF THE CALORIMETER AND CONTENTS WAS ASCERTAINED.

The temperature of the calorimeter was adjusted in the same manner as that described in Appendix I.

The time of transit across five bridge-wire divisions about the readings 50, 60, and 70 centims. was taken, and the times at 50, 60, and 70 deduced. I give particulars of Experiment IV., as that was the one quoted in Appendix I., from which the value of Q_s at 40·1 was deduced.

TABLE XXIII.—Experiment No. IV., September 17.

Number of Clark cells 3 (each consisting of 4 in 11^1). Temperature cells, 15°·14 C.; temperature bridge-wire, 63°·5 Fahr.

Bridge-wire reading.	Time (chronograph).	Revolutions (1000's).	Time.	External temperature by thermometer II.
49	81·7			882·35
49·5	113·6	0	100·1	
50	144·6			
50·5	176·9			
51	207·5			882·39
	144·9			882·37
59	730·5	3	669·0	882·40
59·5	764·1			
60	797·6			
60·5	831·4			
61	865·6	4	858·5	882·40
	797·8			882·40
69	1421·0			882·40
69·5	1456·6	7	1426·6	
70	1493·3			
70·5	1529·0			
71	1565·7			882·40
	1493·1	Time per 1000	189·50 ∴ r_1 = 5·277	882·40

The operations necessary for the reduction of Experiment IV.* are as follows:—

Data required.

Mean value of 1 centim. of range in terms of mean bridge-wire centim. (given by calibration of bridge-wire; see p. 285)—

50 to 60	1·00082
60 to 70	·99551.

Correction for temperature bridge-wire to 15° C. = range $\{1 + \cdot 00016\ (\text{F.}^\circ - 59)\}$

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* Fuller particulars concerning this method of reduction will be found in Paper A.

1 millim. of No. II. = 5·51 millims. of bridge-wire, and 882·40 millims. = 40°·142. Bridge-wire null-point = 599·55 millims.

Range.	Time over range.	Change temperature on therm. II.	Resulting change range.	$d\theta_1/dt \times 10^4$.	Correction to mean bridge-wire. $\times 10^4$.	Correction for temperature C. cells and bridge-wire $\times 10^4$.	Corrected $d\theta_1/dt$ $\times 10^4$.
centims. 50 to 60	652·9	+·03	+·16	1533·9	+1·3	+·4, +1·1	1536·7
60 to 70	695·3	0	0	1438·1	−6·4	+·3, +1·0	1433·0

Hence we get ·15367 and ·14330 as the values of $(d\theta_1/dt)_{es}$ at 55 and 65 centims. respectively. We can thus deduce the value at the null-point (599·55). We get ·14853.

Now (Appendix I.) the value of $(d\theta_1/dt)_s$ for rate 5·277 = ·00158, therefore $(d\theta_1/dt)_{3e}$ = ·14695.

Now $\left(\frac{d\theta_1}{dt}\right)_{3e} \times \frac{R_1 \times C_b}{(ne)^2}$ gives the rise per second in degrees C. with unit resistance and unit potential difference, where R_1 is the resistance in true ohms of the coil at temperature θ_1, n the number of Clark cells of P.D. e volts, and C_b the value of the mean bridge-wire millim. at 15° C. when $\theta_1 = 40^\circ{\cdot}1$, expressed in terms of the N thermometer (see p. 289). Hence if T is the time of rising 1° C., we get

$$T = \frac{(ne)^2}{(d\theta_1/dt)_e \times R_1 \times C_b},$$

and

$$R_{3e} = 10{\cdot}377 \text{ (see Table VIII.)}, \quad (ne)^2 = 18{\cdot}513, \text{ and } C_b = {\cdot}009100,$$

therefore

$$T = 1334{\cdot}1,$$

and

$$C_{\theta_1} = \frac{T}{J} \text{ (where } C_{\theta_1} \text{ is capacity for heat at } \theta_1\text{), and } J = 4{\cdot}199,$$

therefore

$$C_{\theta_1} = \mathbf{317{\cdot}82} \text{ thermal grams.}$$

The following table gives the results of all the experiments made with the object of obtaining the values of C_{θ_1}.

TABLE XXIV.—Determination of the Capacity for Heat of Calorimeter and Contents.

No. of Expt. and date.	Mean bridge-wire reading.	$\left(\frac{d\theta_1}{dt}\right)_{es}$ corrected $\times 10^4$.	Temp. C.	$\left(\frac{d\theta_1}{dt}\right)_{es}$ at N.P. $\times 10^4$.	Stirring rate.	$\left(\frac{d\theta_1}{dt}\right)_s$ $\times 10^4$.	$\left(\frac{d\theta_1}{dt}\right)_3$.	R_{3e} (App. III.).	$(ne)^2$.	C_b $\times 10^6$.	$T = \frac{ne^2}{\left(\frac{d\theta_1}{dt}\right)_{3e} \times R_1 \times C_b}$.	$\frac{T}{J} = C_{\theta_1}$.
III. Sept. 10	55 65	1492·9 1389·1	50·024°	1441·2	5·688	−11·0*	·0014302	10·403	18·513	9128	1363·3	324·74†
II. Sept. 10	55 65	1534·5 1430·4	40·122	1482·9	5·742	−22·2	·0014607	10·378	18·513	9100	1342·1	319·74†
IV. Sept. 17	55 65	1536·7 1433·0	40·142	1485·3	5·277	−15·8	·0014695	10·377	18·513	9100	1334·1	317·88
I. Sept. 10	57·5 63·75	1540·6 1477·7	31·996	1516·1	5·534	−26·2‡	·0014899	10·356	18·513	9078	1321·9	314·87†
V. Oct. 5	55 65	1575·7 1477·3	29·979	1527·2	5·328	−24·0	·0015032	10·351	18·513	9073	1311·5	312·41
VI. Oct. 5	55 65	1586·3 1473·4	29·998	1530·7	5·489	−27·0	·0015037	10·351	18·513	9073	1311·1	312·35
VII. Oct. 21	55 65	1619·2 1515·2	20·031	1568·3	5·438	−33·2*	·0015351	10·328	18·513	9046	1291·0	307·50

* The value of $\left(\frac{d\theta_1}{dt}\right)_s$ in Experiments III. and VII. is somewhat doubtful, although it is probably accurate to 1 in 50 (see Appendix I.).

† The capacity for heat of the calorimeter during Experiments I., II., and III. was greater by 1·6 than during the remaining experiments.

‡ The value of $\left(\frac{d\theta_1}{dt}\right)_s$ in Experiment I. is taken from the curve through the values at the other temperatures. I made no direct stirring experiments at 32°.

In Paper A. I have given a full account of the determination of the "water equivalent" (W_1) of this calorimeter, and I have every confidence in the values there given.

From Table VI. of that Paper I extract the following :—

θ_1	W_1.
°	
20	80·11
30	80·90
40	82·19
50	83·39

During these experiments, the silver flask contained a mercury thermometer (G_2) which was used, during my earlier L experiments, to indicate the internal temperature of the flask. As described (*ante*), a metal conical tube had been cast on to the stem of this thermometer by means of the alloy, and the tube carefully ground into the neck of the flask to prevent any diffusion of vapour up the glass tube, down which the thermometer passed. After I adopted the "exhaust" method of performing the L experiments, this thermometer was removed from the apparatus; this occurred between Experiments III. and IV., Table XXIV. I had forgotten the circumstance, and when I reduced the results, I was much troubled as to the different values of C_{θ_1} given by Experiments II. and IV., which were at about the same temperature. It was some time before the cause of the discrepancy suggested itself to me. I then obtained an approximation to the capacity for heat of thermometer G_2 and tube, as follows : The temperature of both calorimeter and tank being steady, the bridge was adjusted until the galvanometer ceased to swing. Thermometer G_2 was then suspended above the tube communicating with the flask, and its temperature read by the reading microscope. It was then rapidly lowered into its place, and observed until its temperature became steady (this took place in about 4 to 5 minutes). The tank being at 40° and the external temperature about 20°, the thermometer rise was about 20°, and a small error in reading was of little consequence. The bridge contact-maker was then re-adjusted, and the change in temperature of the calorimeter deduced from the difference in the readings. Hence the capacity for heat of G_2 could be found. Four experiments were performed with the following results :—

(1)	1·52
(2)	1·65
(3)	1·62
(4)	1·58
Mean . .	159

If we assume the capacity as 1·6, we cannot be greatly in error, and this quantity must be subtracted from the values of W_1 (*supra*) for all experiments after No. 3. Now the values of C_{θ_1} from Experiments II. and IV. differ by 1·89. This apparent difference of ·3 in the results has, however, to be further diminished. On September 14, I found it necessary to withdraw thermometer AB from the calorimeter. Before doing so, I weighed a "weighing bottle" containing a roll of blotting-paper, and on removing the thermometer, I wiped its stem and bulb with this paper in order to find the weight of oil withdrawn, which proved to be ·104 gram. Hence the differences in Column VI. of the next Table.

TABLE XXV.—Specific Heat of Oil.

I. Experiment.	II. Temperature.	III. C_{θ_1} (Table XXIV.).	IV. W_1 (*supra*).	V. Cap. of oil.	VI. Wt. of oil (*vacuo*).	VII. s_1.
III.	50·024°	324·74	83·39	241·35	474·12	·5090
II.	40·122	319·74	82·20	237·54	474·12	·5008
IV.	40·142	317·88	80·60*	237·28	474·02†	·5005
I.	31·996	314·87	81·14	233·73	474·12	·4930
V.	29·979	312·41	79·30*	233·11	474·02†	·4917
VI.	29·998	312·35	79·30*	233·05	474·02†	·4916
VII.	20·031	307·50	78·51*	228·99	474·02†	·4830

Appendix III.—DETAILS OF DETERMINATION OF R_1.

In Paper J., p. 409, is given a table showing the errors of all the individual coils in my dial resistance box. These errors were, by kind permission of Mr. GLAZEBROOK, ascertained by direct comparison with the B.A. standards.

I extract the following from the remarks on that table (p. 410, *ibid.*):

"A table was constructed giving the total difference between the reading and the real value (in terms of "legal ohms") for every position of the plugs in each dial. This difference we termed the "plug correction."‡ Having made this correction, we had then to correct for any inaccuracy in the ratio arms of the bridge, and as all determinations of the calorimeter coil resistance were made with 1000 (right) and 10 (left) as the arms, it is only necessary to here give the correction for those coils.

"Now

$$10L/1000R = 9{\cdot}9977/1000{\cdot}30 = 0{\cdot}0099947.\S$$

---

* After removal of thermometer G_2.

† After removal of ·10 gram oil.

‡ The correction for the temperature of the coils was made before applying the "plug correction."

§ There is here a mistake in Paper J. This was corrected in a subsequent communication, 'Proc. Roy. Soc.,' vol. 55, p. 25.

"This we termed the "bridge correction."

"The resulting values are expressed in legal ohms, and true ohms = reading in legal ohms (1 − ·0024275)."

The above extract is sufficient to explain the operations. I now give a complete example of a determination of R_1 and the subsequent calculations.

The value of θ_0 we obtained by direct observation of thermometer II., and d' by observation of the bridge reading. Then $\theta_1 = \theta_0 + d'$.

TABLE XXVI.—Determination of Coil Resistance. October 11.

See p. 296.	Galvanometer swings.*	Observed R.	Temperature coils.	R + r.	Correction for temperature coils.	Plug correction.	R + r (box ohms).
N_1	331 170 191 341 140 171	$58\frac{140}{311}$	..	58·450	+·002	+·007	58·459
N_2	417 296 222 350 195 54	$1095\frac{195}{249}$	17°·08	1095·783	+·033	+·777	1096·583
N_3	407 281 201 322 206 41	$1095\frac{206}{247}$	..	1095·834	+·033	+·777	1096·634
N_4	282 128 173 329 109 201	$58\frac{109}{310}$	..	58·352	+·002	+·007	58·361

As previously remarked, the difference in the resistance of the leads accounts for the difference between N_2 and N_3, and N_1 and N_4.

We thus get

$$R_1 + r = \{(N_2 + N_3) - (N_1 + N_4)\} / 2 = 10{\cdot}38199 \text{ box ohms.}$$
$$= 10{\cdot}37648 \text{ "legal" ohms.}$$
$$= 10{\cdot}35128 \text{ true ohms.}$$

Reading of thermometer No. II. = 684·77 millims. = 29°·997 C.
,, bridge-wire = 590·1, and null-point = 599·25 (see p. 288).

Therefore

$$d' = -\ {\cdot}084^\circ \text{ C.}$$

---

* Resistance in battery circuit (2 Leclanchés) = 700 ohms when observing N_2 and N_3, and 2900 ohms when observing N_1 and N_4.

Hence $\theta_1 = 29^\circ{\cdot}913$ and $R_1 + r = 10{\cdot}3513$ true ohms.
therefore, when $\theta_1 = 30^\circ{\cdot}000$ $R_1 + r = 10{\cdot}3515$ „ „

The values of $R_1 + r$ at about 30° were also ascertained on other dates, and were as follows :—

Date.	Temperature.	$R_1 + r$.	$R_1 + r$ at 30°.
September 15	° 30·003	10·3516	10·3516
October 5	30·245	10·3522	10·3516
„ 10	30·044	10·3518	10·3517
„ 11	29·913	10·3513	10·3515

I think it unnecessary to multiply examples at other temperatures, the above will show the order of accuracy.

From the above values, the value of r (= ·0034, see p. 296) must be subtracted in each case to get the value R_1, given in Table VIII., p. 297.

Description of Plates 4, 5, and 6.

PLATE 4.

The lower figure is a vertical section of the steel chamber and tank. The spaces filled with mercury are printed in black. The tube at D communicated with the regulating apparatus.

The upper figure is a plan of the lid.

PLATE 5.

Fig. 1 is a vertical section of the calorimeter. When gas was driven through the apparatus it entered at *f*, passed into the bottom of the silver flask F at G and left it near the roof at *d*. It descended to the bottom of the 18 ft. silver coil (sections of which are shown by the small circles at C_2), then ascended a gentle slope and finally left the calorimeter by the tube *c*. Although in different planes from the section, the position of the platinum thermometer is indicated as well as S, the bottom of the stirrer. A "dropper" is shown in position in the tube *h*.

Fig. 2 is a horizontal section across the calorimeter at AB in fig. 1.

Fig. 3 is a plan of the lid.

The stirring shaft passed through S, the platinum thermometer down T, and the tube *h′* established communication with the flask F (fig. 1). The ends of the silver spiral are shown at *c* and *f*.

Fig. 4 shows the method of insulating the leads where they passed through the lid of the calorimeter at *l* and *l′* (fig. 3), and also the insulation of the four leads where they passed through the steel lid (see small sketch, Plate 6, fig. 3).

PLATE 6.

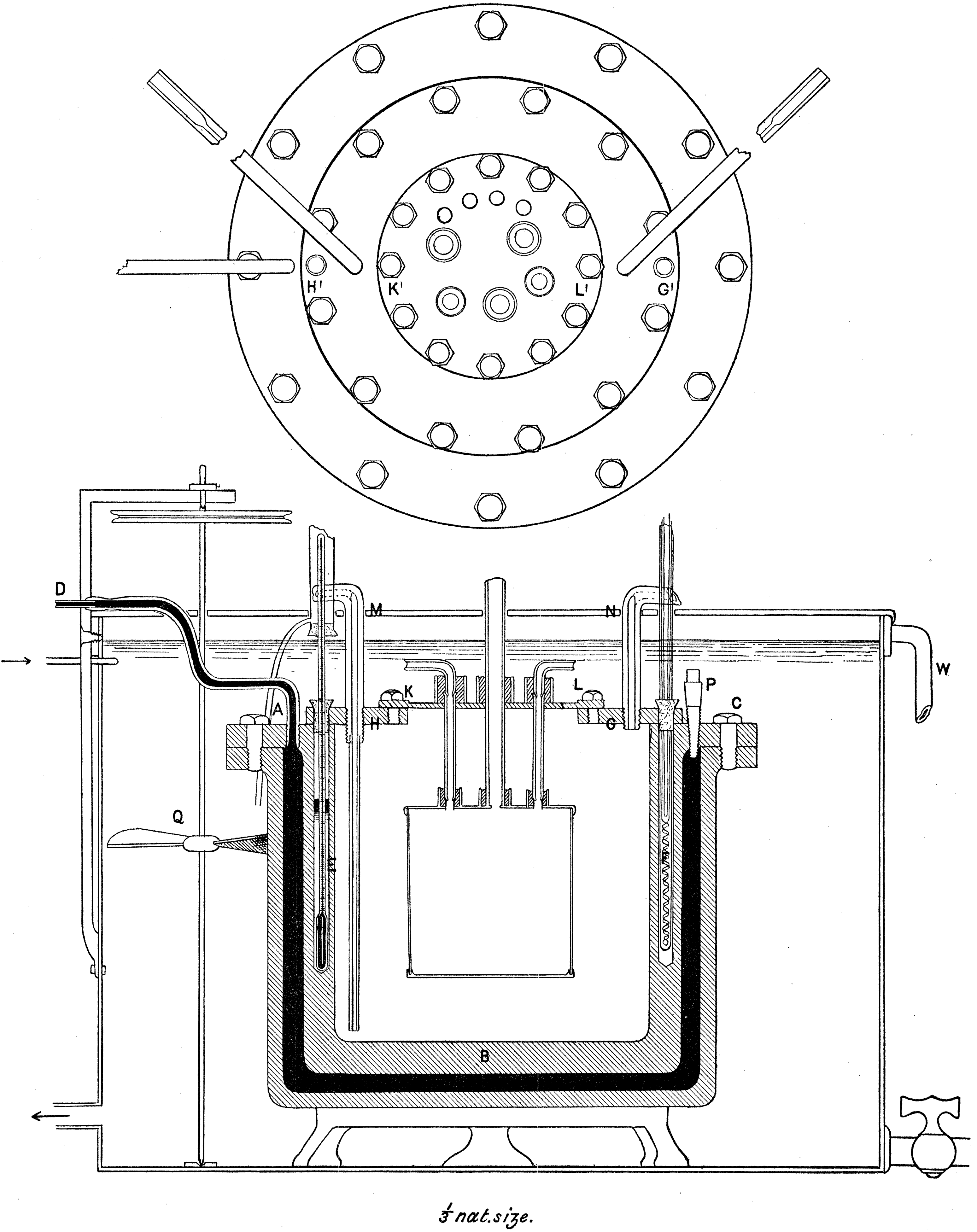
Fig. 1 is diagrammatic only, for the various tubes, &c., repeatedly crossed each other. The gas on entering passed through H_2SO_4 at S, then through P_2O_5 at P, afterwards through the 30 ft. coil indicated at C, and thus attained to the temperature of the tank water. M_1 is an open scale manometer to show the pressure of the gas when entering the flask F. Leaving this flask near the top, the vapour traversed the coil C_2 and thus attained the temperature of the calorimeter; it then passed through the four-way tap T_4, and on emerging from the tank passed over a row of small gas jets, shown at G. The tubes between T_4 and B could be swept by dry air, by use of the taps T_2 and T_4. All the apparatus within the dotted lines was immersed in the tank water.

Fig. 2 shows the arrangements of the differential thermometers and the bridge. The coil of AB is in series with the compensators of CD and *vice versâ*.

Fig. 3 shows the electrical connections with the calorimeter coil.

A coil in the tank at F was of the same resistance and wire as the calorimeter coil. By means of the key K_1 the current could be switched on to either coil. K_1 was also connected with the chronograph in such a manner that all its movements were recorded.

By means of the Rheochord the external resistance of the storage circuit (leads 2 and 4) could be so adjusted that the D.P. at the points M and N was always that of the Clark cells. Wires numbered 1 and 3 are in the Clark cell circuit.



⅓ nat. size.

Calorimeter.

3/4 nat size.

Section.

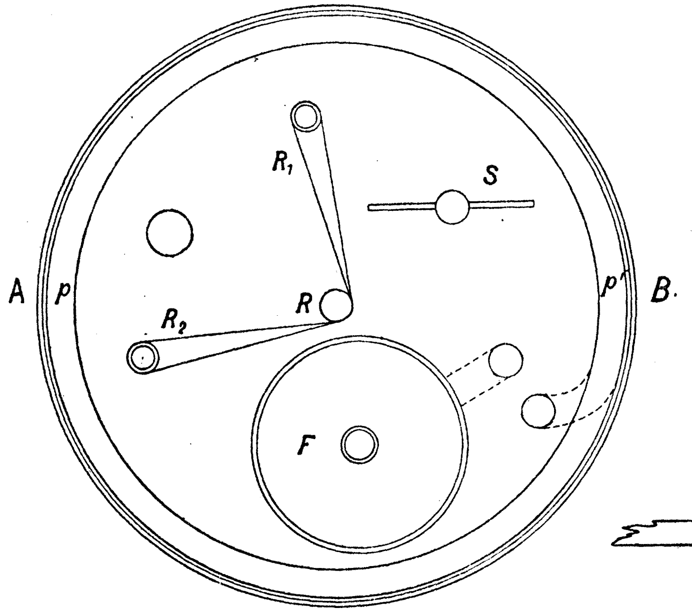


Fig. 2.

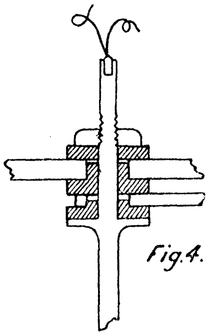


Fig. 4.

Lid.

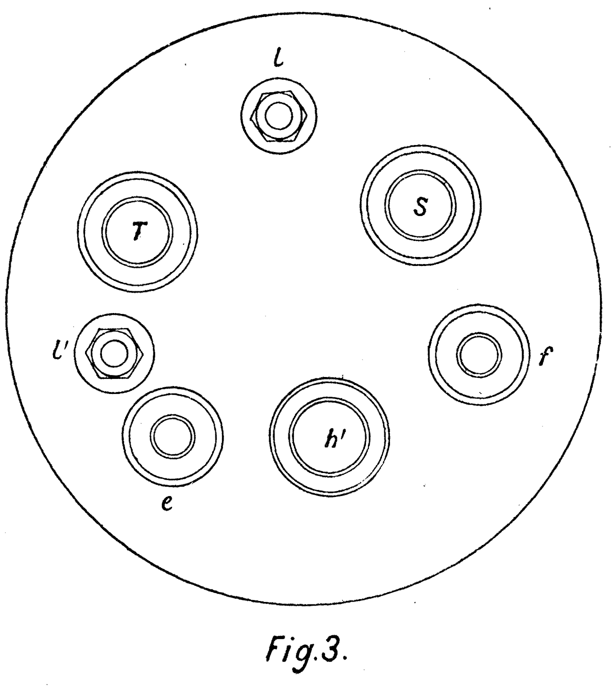


Fig. 3.

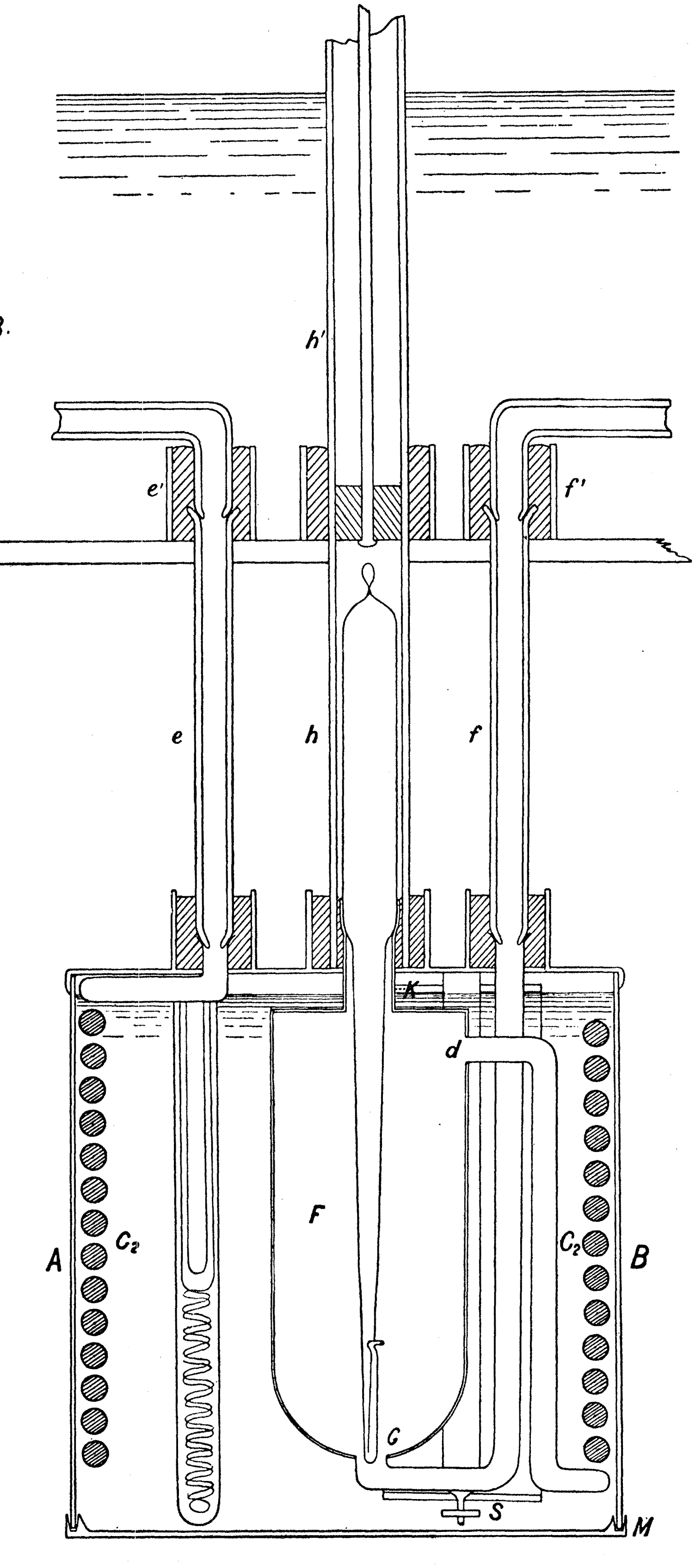
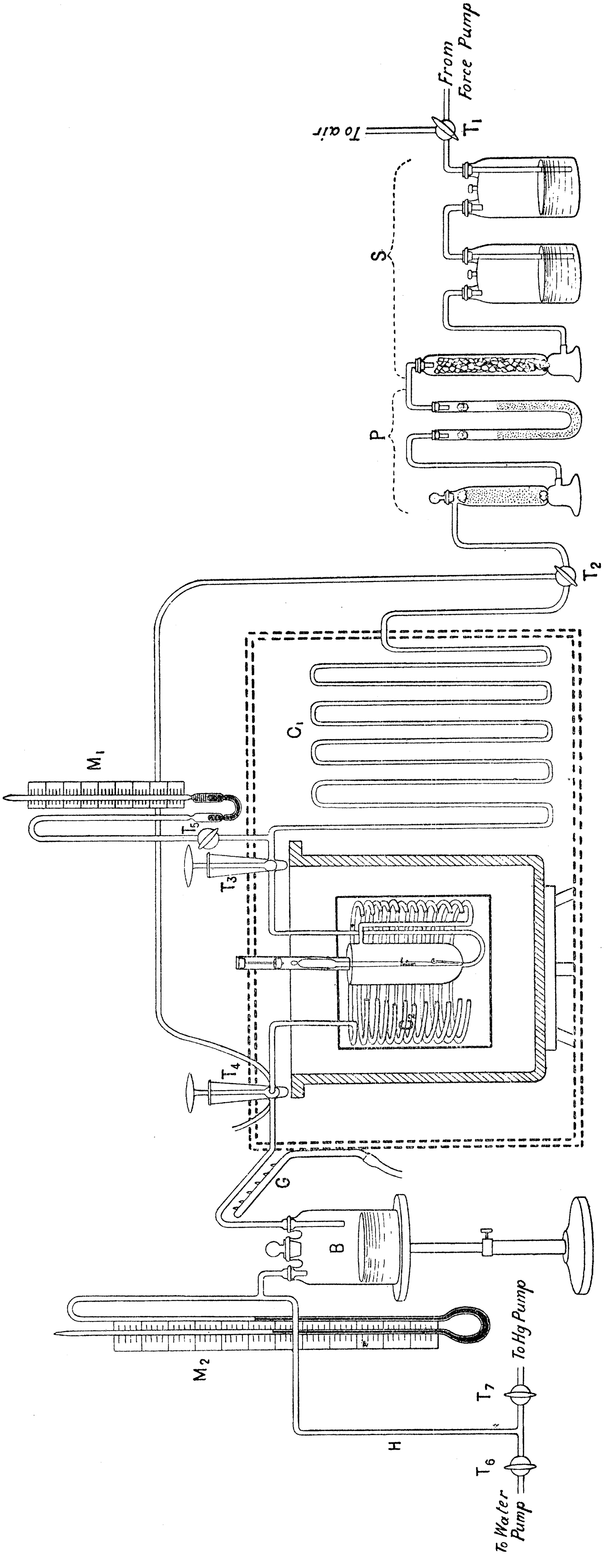


Fig. 1.



Diagrammatic View of Gas Circuit. Fig. 1.

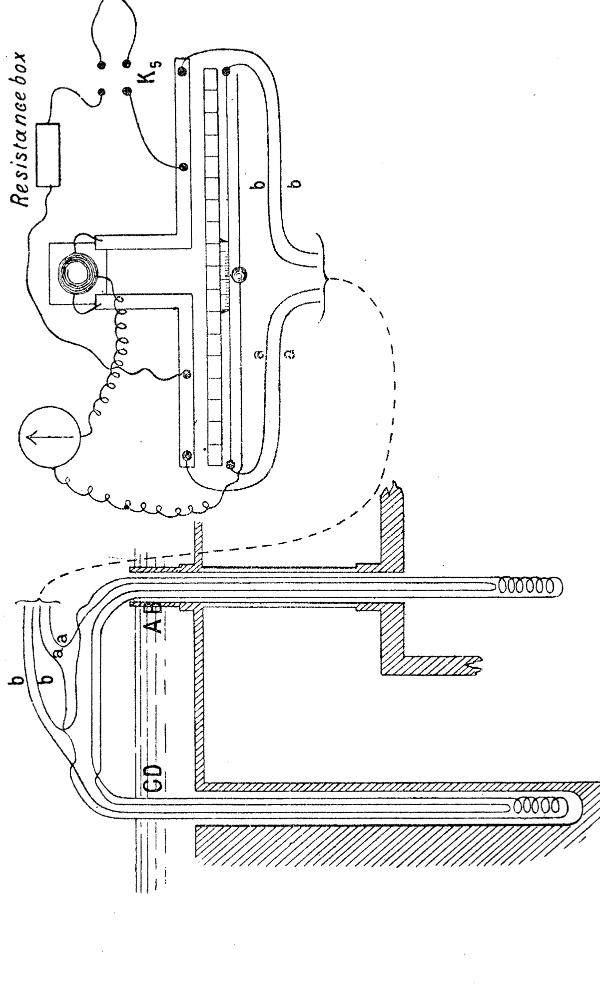


Fig. 2.

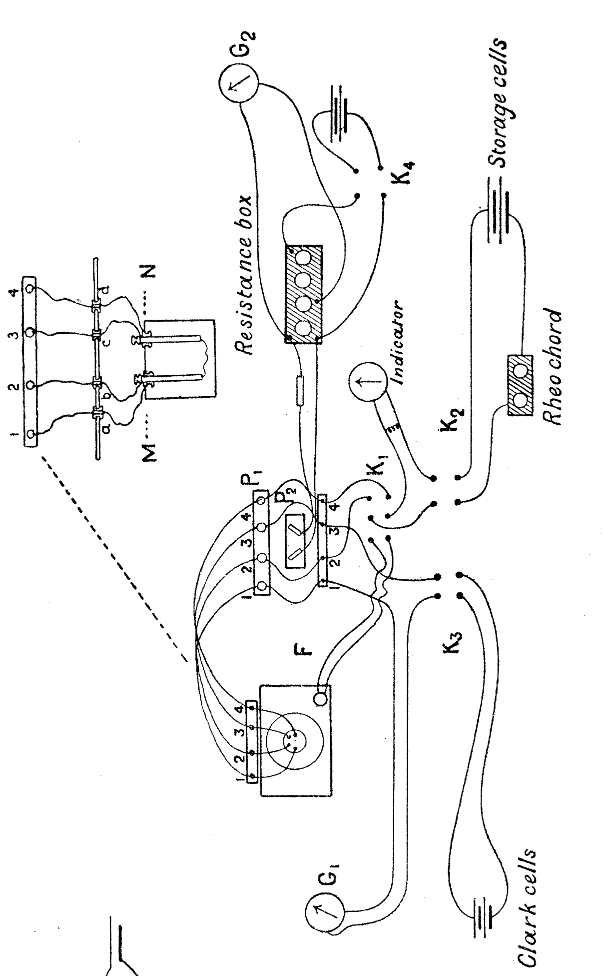


Fig. 3.
Electrical Connections.