

## The Latent Heat of Evaporation of Benzene

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slide-rule, for it performed the function of a slide-rule, in which the graduations of the slide were made on indiarubber, so that the ratio of the length of the scale on the rule to the length of the scale on the slide might be altered at will, and thus involution and evolution with fractional indices performed.

Prof. S. P. THOMPSON and Mr. TROTTER expressed their admiration for the author's method of "stretching" the scale.

Mr. BURSTALL said he had attempted to apply a similar method to the Fuller rule, but did not succeed, since in this rule there was only one scale. He hoped the author's method could be applied in a form such that a greater accuracy than 1 in 300 could be obtained.

Mr. BOURNE thought the fact that the point of intersection of two lines inclined at an acute angle had to be read was likely to limit the accuracy.

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III. *The Latent Heat of Evaporation of Benzene.* By E. H. GRIFFITHS, M.A., F.R.S., *Sidney Sussex College, Cambridge*, and Miss DOROTHY MARSHALL, B.Sc., *University College, London*\*.

1. THE method of experiment and the nature of the apparatus employed have been fully described in previously published papers. Although it appears somewhat presumptuous to assume, on the part of the reader, a knowledge of such communications, it would on the other hand seem redundant to devote many pages to the mere repetition of what has already appeared in print. We therefore propose to give an explanatory statement of the theory and methods employed, but to omit all detailed description of the apparatus. Full references to former communications will be given when necessary, so that all particulars can be ascertained by any who desire them.

\* Read November 8, 1895.

As reference has frequently to be made to the following papers (by E. H. Griffiths) they are, for convenience, denoted as follows :—

Paper J. "The Mechanical Equivalent of Heat," Phil. Trans. vol. clxxxiv. 1893, A, pp. 361–504.

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

Paper W. "The Latent Heat of Evaporation of Water," Phil. Trans. vol. clxxxvi. 1895, A, pp. 261–341.

## 2. *Description of the Method.*

In order to render our account of these experiments intelligible, we find it necessary to give the following somewhat lengthily extract from Paper W, pp. 270–273 :—

"The method adopted was of such a nature that the 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. ;

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  $L$  is small as compared with the changes in  $\theta$ . 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 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 liquid to be evaporated was contained 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 a certain singularly limpid oil consisting of hydrocarbons only.

“The calorimeter (which was filled to the roof with the 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  $\frac{1}{100}^{\circ}$ ), 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 it will be found 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,

and it was in the estimation of this 'stirring supply' that the greatest difficulties were encountered. 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 even if the value of the E.M.F. of the Clark cells, or the absolute resistance of the box-coils given by the standardizations performed during the determinations of  $J$ , is in any way inaccurate, such errors would now 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 the value of  $J$  obtained by the use of these standards, we get the comparison in terms of a thermal unit at  $15^{\circ}\text{C}$ ., independently of the numerical value assumed in the reductions.

"One further correction remains to be noticed. The temperature of the calorimeter has been referred to 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 usually small, and in any case could be determined with great accuracy.

"Having indicated the nature of the observations, we 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;

$Q_m$  be the thermal units per second due to the mechanical supply;

$\Sigma q$  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  $\theta$ , and if the electrical supply is maintained for a time  $t_e$ , and the mechanical for a time  $t_m$ ,

$$ML = Q_e t_e + Q_m t_m + \Sigma q. \quad \dots \quad (1)$$

"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  $\theta_1$ , then

$$Q_s = \frac{e^2 n^2}{R_1 J} \dots \dots \dots (2)$$

"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  $\Sigma q$  would vanish; but although this term throughout these experiments was of small dimensions, it could not be entirely ignored.

"Let  $\theta_0'$  and  $\theta_0''$  be the temperature of the surrounding walls at the beginning and end of an experiment; suppose the calorimeter temperature ( $\theta_1$ ) 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  $C_{\theta_1}$  is the capacity for heat of calorimeter and contents at the temperature  $\theta_1$ .

"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

$$\Sigma q = C_{\theta_1} \{(\theta_0' - \theta_0'') + (d' - d'')\}^*. \dots (3)$$

Hence

$$ML = \frac{e^2 n^2 \times t_s}{R_1 J} + Q_s \times t_s + C_{\theta_1} \{(\theta_0' - \theta_0'') + (d' - d'')\}. \quad (4)''$$

\* 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  $\theta_0'$ ,  $\theta_0''$ ,  $d'$ , and  $d''$ , the actual temperature of the calorimeter at any time could only be obtained in this manner.

3. The following table shows the *comparative* mean values of the terms in equation (4) resulting from our experiments on benzene\*.

TABLE I.

No. of Cells.	$Q_E t_E$ .	$Q_S t_S$ .	$\Sigma q$ .
5	1	·008	$\pm \cdot 005$
4	1	·011	$\pm \cdot 009$
3	1	·015	$\pm \cdot 001$

We found that the thermal balance was most easily maintained when the potential-difference was that of 4 cells, therefore the majority of our experiments were performed with that potential-difference, the experiments with 5 and 3 cells being used as a check upon the results. To secure an accuracy of (say) 1 in 1000 in the total heat-supply, the above table shows that it was necessary to measure

$Q_E t_E$  to (say) 1 part in 2000,

$Q_S t_S$  „ 1 „ 15,

$\Sigma q$  „ 1 „ 10;

but as the sign of the last term was in some experiments positive, in others negative, the above degree of accuracy was not essential, since, when taking the mean of a number of observations, the effect of any error in  $\Sigma q$  would be greatly diminished. We believe that the above order of accuracy was exceeded in the measurement of the respective terms. In the case of the experiments with 3 cells at  $20^\circ$  an order of accuracy of 1 in 50 would be required in the value of  $Q_S t_S$  to secure the same standard; hence we do not regard our determinations at that temperature as possessing an equal authority with those at higher temperatures.

\* (Experiments Preliminary, XIX. a, XXXV., and XXXVI. were not included when calculating this table, as they are in several respects exceptional.)

#### 4. *The Method of maintaining the Space surrounding the Calorimeter at a Constant Temperature $\theta_0$ .*

A full description of the somewhat elaborate apparatus designed for this purpose will be found on pp. 374-378 of Paper J, and some improvements which were subsequently added are described on pp. 274-276 of Paper W. This portion of the apparatus did not, for some unknown reason, appear to be working with the same perfection this year as it did in the summer of 1894. Oscillations in  $\theta_0$  (the external temperature), amounting to  $\frac{1}{100}^{\circ}\text{C.}$ , were on several occasions observed, the greatest change during the whole series being  $\cdot 0145^{\circ}$ . This, however, was exceptional and, as an inspection of our final tables will show, the change in the course of an experiment (*i. e.* in about half an hour) was usually only about a few thousandths of a degree at temperatures varying from  $20^{\circ}$  to  $50^{\circ}\text{C.}$ ; the constancy of  $\theta_0$  was therefore sufficient for our purpose.

Had it been possible, we should have preferred to determine  $\theta_0$  by means of a platinum-thermometer, as we could thus have detected smaller changes; but a third observer would, in that case, have been required, and circumstances did not permit of this addition\*.

The mercury-thermometers used for indicating the temperature of the steel chamber in which the calorimeter was suspended were graduated in millimetres, and had been carefully calibrated and compared with two Tonnelot thermometers standardized at the Bureau International†. The stems of these thermometers (where they projected above the tank-lid) were surrounded by glass tubes up which a stream of tank-water was forced by means of a pump driven by a water-motor: thus the stem-temperature was always that (or nearly that) of the tank, and the readings were not affected by changes of temperature in the room. The actual value of  $\theta_0$  was of small consequence, an accuracy of  $\frac{1}{10}^{\circ}\text{C.}$  being

\* We believe that such irregularities as present themselves in our final results are partly due to the employment of mercury-thermometers for the determination of the changes in  $\theta_0$ .

† See "The Measure ment of Temperature," Science Progress, Sept. 1894.



sufficient ; but it was necessary to read *changes* of temperature during an experiment to nearly  $0^{\circ}\cdot001$  C., and this we believe we were able to do. A full description of the various precautions taken will be found in Paper A, pp. 55 and 56, and Paper W, pp. 275, 276.

The observations were taken by means of a reading-telescope fitted with a micrometer-eyepiece, which directly divided 1 millim. on the thermometer-stem into 10 parts : thus  $0\cdot1$  of a millimetre could be directly read, and  $\cdot01$  could be estimated. There is no doubt that the actual readings could be taken to  $\cdot025$  millim., that is about  $0^{\circ}\cdot001$  C.

Thermometer A had a range of  $16^{\circ}$  to  $26^{\circ}$  C., and about 27 millim. were equivalent to  $1^{\circ}$  C.

Thermometer II. had a range of  $28^{\circ}$  to  $53^{\circ}$  C., and about 20 millim. were equivalent to  $1^{\circ}$  C.

All temperatures, both when obtained from these and from the platinum-thermometers, are throughout this Paper expressed in terms of the nitrogen-scale.

##### 5. *The Calorimeter and its Connexions.*

A full description will be found on pp. 276–281 of Paper W, and drawings and sections on plates 5, 6 of the same paper. The brief account given in the description of the method *supra* is sufficient to indicate the nature of the arrangements to those who are not familiar with that paper.

The *differences* of temperature between the calorimeter and surrounding walls were determined by means of differential platinum-thermometers. A description of the method of standardization and observation of those thermometers is given on pp. 52–56 of Paper A, and some further details on pp. 285–290 of Paper W. Experimental evidence is there adduced in support of the following statement :—“ It follows that differences of temperature could be determined to  $\cdot0004^{\circ}$ , and differences of  $\cdot0001^{\circ}$  could be detected.”

The following Table shows the difference in temperature corresponding to a difference of 1 mean millim. of the bridge-wire whose opposite ends were connected with the thermometers :—

TABLE II.

Temp.	$\Delta\theta$ for difference of 1 mean millim. bridge-wire.
26	0.009046
30	0.009073
40	0.009101
50	0.009128

By experiments repeated this summer we found that no change had taken place in the value of the mean bridge-wire millimetre. A slight change (particulars of which are given in a subsequent section) had, however, occurred in the position of the null-point, *i. e.* in the reading on the bridge-wire when the temperature of the two thermometers was identical.

6. *Brief Description of the Method of obtaining the Value of the Terms in the Expression*

$$\text{Total heat} = Q_{\text{e}} t_{\text{e}} + Q_{\text{s}} t_{\text{s}} + \Sigma q.$$

$$Q_{\text{e}} t_{\text{e}} = \frac{(ne)^2 \times t_{\text{e}}}{R_1 \times J}.$$

The ends of the platinum-silver coil (immersed in the oil surrounding the evaporating-flask and spiral) were kept at a constant potential-difference by means of the arrangements described in Paper J, pp. 382-388. This potential-difference was always some integral multiple ( $n$ ) of the potential-difference of a Clark cell ( $e$ ). During the spring of this year the Clark cells used were again compared with the Cavendish standard ( $R_1$ ), which has shown no signs of change since its standardization by Lord Rayleigh in 1883 and by Messrs. Glazebrook and Skinner in 1891.

The mean value of the whole set of 30 cells differs from  $R_1$  by 0.00004 volt only; and although individual cells show larger discrepancies than in previous years, their mean potential-difference at 15° C. may be taken as 1.4342 volts (see Paper W, p. 297). A number of these cells were always placed in parallel arc: thus when  $n$  is given as 4, we were

really using 12 cells as four files of 3 each. The arrangement for keeping the temperature of these cells at nearly  $15^{\circ}\text{C}$ . has been described in Paper J, p. 385. During the period covered by our experiments, some of the days were extremely hot, and the tap-water became so warm that when turned on by the regulator it was unable to keep down the temperature sufficiently. The extreme range in the temperature of the cell-tank during these experiments was from  $14^{\circ}\cdot 8$  to  $16^{\circ}\cdot 3\text{C}$ . As, however, the movement was always extremely slow, it is probable that the tank-temperature closely corresponded to the effective temperature of the cells, and hence the correction

$$e = 1\cdot 4342\{1 + (15 - \theta) \times 0\cdot 00077\}$$

applied by us gave the value of  $e$  with sufficient accuracy.

The time  $t_x$  was determined by means of a chronograph controlled by an electric clock, whose gaining rate is now less than 1 in 20,000. Any movement of the keys by which the current was switched on to the calorimeter-coil was automatically recorded on the tape; and thus personal errors were eliminated. The times could have been read to  $\frac{1}{100}$  of a second, but it was considered unnecessary to read to nearer than  $\frac{1}{10}$ , *i. e.* about 1 in 7000 of  $t_x$ .

The value of  $R_1$  is expressed in terms of the "true ohm" as given by the B.A. standards, with which (by kind permission of Mr. Glazebrook) the coils used by us have been directly compared (Paper J, pp. 407-410).

The increase in  $R_1$  due to the rise of temperature caused by the current was determined in the manner described in Paper J, pp. 404-407 (see also Paper W, p. 296).

The value of  $J$  assumed by us was  $4\cdot 199$  (Paper W, p. 314). We would emphasize the fact to which attention has been previously directed (section 2, p. 3), namely, that even if, in consequence of errors in the standards &c., this value of  $J$  is incorrect, it is still the right value to use for the reduction of these observations, for, provided that no change has taken place during the past three years in the standards used (and direct comparisons show no signs of any change which would affect the results), the values of  $L$  obtained by us are independent of the numerical values of  $J$  and  $R$  when expressed in terms of

the same units as those assumed during the determination of the mechanical equivalent.

The value of  $Q_s t_s$  is thus expressed in terms of a "thermal unit at 15° C."

#### 7. $Q_s t_s$ .

The method adopted for finding  $Q_s$  (the thermal units per second due to the work done by stirring) has been fully described in Paper W, pp. 290–293. It was there shown that the value of  $Q_s$  varied approximately as  $r^4$  (where  $r$  was the rate of revolution of the stirrer), and that this relation was sufficiently close for the reduction of experiments in which the value of  $r$  was somewhere between 5 and 6 per second.

The value of  $Q_s$  was found to increase rapidly as  $\theta_1$  (the temperature of the calorimeter) diminished. Our recent re-determinations of  $Q_s$  have explained a discrepancy which caused an uncertainty in the former determination of  $Q_s$  at 20° and 50°, and we now find that it was due to an arithmetical error in the reduction of the observations. Fortunately, the resulting correction in no way affects the conclusions arrived at in Paper W; and our present investigation confirms the accuracy of the experimental determinations of  $Q_s$  obtained in 1894. As the extreme differences between any of our determinations of  $Q_s$  at temperatures above 20° (after the arithmetical corrections at the 20° and 50° points) do not exceed 1 part in 70, even if we include the values found in 1894, and as the mean probable error at any temperature is much below 1 in 100, it is obvious that the values of  $Q_s$  have been ascertained with more than sufficient precision.

$$8. \Sigma q = C_{\theta_1} \{(\theta_0' - \theta_0'') + (d' - d'')\}.$$

We have previously indicated (sect. 4, p. 6) the manner in which  $\theta_0'$  and  $\theta_0''$  (the initial and final temperature of the walls of the surrounding chamber) were determined by the direct observation of mercury-thermometers. The value of  $d$  (the difference between  $\theta_1$  and  $\theta_0$ , *i. e.* the calorimeter-temperature and that of the surrounding walls) was ascertained by the differential platinum-thermometers previously referred to, and was always small—rarely greater than .01° C. It was usually determined by the reading of the galvanometer-swings

without altering the position of the contact-maker on the bridge-wire.

When evaporating water, the values of  $d$  were so small that an approximate value of the swing (in terms of a length of the bridge-wire) was sufficient. During these benzene experiments, however, we found it impossible to maintain the thermal balance with such perfection. The only values of  $d$  which were of consequence were  $d'$  and  $d''$  (the initial and final values), and, especially in the earlier experiments, the internal temperature ( $\theta_1$ ) rose so rapidly as soon as the last drop of benzene had evaporated, that it was found impossible to switch off the electric current from the calorimeter-coil at the precise moment necessary to reduce  $d''$  to negligible dimensions. As a consequence, the final swings (which were read by means of a micrometer-eyepiece) were often considerable, and therefore it was necessary to determine their value on each occasion; for, although throughout a series of experiments at the same temperature the value varied but little, the changes were sufficient to affect the resulting value of  $\Sigma q$  in exceptional cases. In the earlier experiments, especially from Preliminary to No. VII., when the difficulty of the final adjustment had not been fully realized, the values of  $d''$  were unduly large, and their equivalent degree-measurements are therefore somewhat doubtful, owing to insufficient determinations of the value of the galvanometer-swings. We feel sure, however, that from No. VII. onwards any errors due to this cause must be very small—certainly not so great as 1 in 50; for the value of a swing of 100 (in terms of a millim. of the bridge-wire) would, throughout a group of experiments at the same temperature, vary (for example) from 1.31 to 1.34 millim.\* This change in value would produce no appreciable effect on  $\Sigma q$  when the difference between the initial and final swings did not exceed 50 or 60, as was the case in most of our later, and better, experiments.

The value of  $C_{\theta}$ , (capacity for heat of calorimeter and contents) remains the same as last year with the exception that 0.1 gram. of the oil was removed at the commencement of July when withdrawing the platinum thermometer for purposes

\* 1 millim. of the bridge-wire indicated a temperature-difference of about  $0^{\circ}.009$  C.



(termed by us a "dropper") narrowed at its open extremity to a capillary tube, which was doubled back on itself for rather over 1 cm., and again bent near the open end, so that the last 1 or 2 mm. were horizontal. These droppers varied in capacity from about 4 to  $6\frac{1}{2}$  c.c., and were filled in the following manner:—The dropper (point uppermost) was lowered by a fine wire to the bottom of a tube about  $4\frac{1}{2}$  ft. long, of which the lower 10 inches or so were filled with benzene, while the upper 3 ft. were surrounded by a "condenser-tube" through which tap-water was continually passing. The lower end, containing the benzene, was transferred at regular intervals from a vessel of water at about  $86^{\circ}\text{C}$ . to a vessel of cold water; thus the benzene was alternately boiled and cooled without any escape of vapour into the room. Five or six such transferences were generally required to completely fill the dropper. The containing tube was then placed in a bath at about  $65^{\circ}\text{C}$ . until the temperature of the benzene was steady. The dropper was now removed and allowed to stand in the open air for some time, in order to get rid of any benzene adhering to its surface. Although simple and effective, these operations occupied a considerable time, and, as a rule, the whole of the morning had to be devoted to the filling of the droppers required for the experiments, which were usually performed at night.

Before an experiment the dropper was lowered, by means of a thread passed through a platinum wire sealed into the closed end, into the calorimeter, where it stood in a vertical position. In Paper W (p. 307) it was shown that, when filled with water, the evaporation through the capillary opening between the time of weighing and the commencement of an experiment might be neglected. In the case of benzene, however, it was found that, for several reasons, loss of this kind could not be disregarded:—

- (1) The vapour-pressure of benzene so greatly exceeds that of water at corresponding temperatures that the loss by diffusion through the capillary was appreciable.
- (2) The surface-tension of benzene is so great that the liquid crept up the sides of the capillary to the opening, and the consequent loss by evaporation was increased.
- (3) In order to supply the air necessary for starting the

boiling when the exterior pressure was removed, a capillary tube, closed at one end, had been sealed within each dropper. It was found that this answered very well during some preliminary trials, when the dropper was placed within a glass tube connected with an exhaust pump so that its manner of discharging could be watched; but on a second filling with our purest sample (the first filling having thoroughly cleaned the interior surface of the droppers) no action took place even when the surrounding pressure was reduced to a few millimetres. In order, therefore, that the expulsion of the benzene from the dropper should commence as soon as the external pressure was reduced to the right amount, it was found necessary to leave a very considerable air-bubble within the tube. Precautions had to be taken to prevent the expulsion of the liquid by the alternate contraction and expansion of the air-bubble when the temperature was changed from that of the balance-case to that of the tank.

These difficulties were surmounted in the following manner.

During the process of filling, as above described, the droppers stood in a vertical position, with the doubled over and open end uppermost, and were never inverted after their removal from the filling-tube, at a temperature of about  $65^{\circ}\text{C.}$ , until their insertion into the calorimeter. The coefficient of expansion of benzene is very large, and, on cooling to the room-temperature, the whole of the upper bend together with a couple of centimetres of the neck between it and the body of the dropper was found to be free from benzene. The dropper was then placed in its case and left in a vertical position in the balance-case for, as a rule, some hours, when the small air-space in the enclosing-case no doubt became saturated with the vapour and thus further evaporation ceased. After being weighed, the dropper and case were lowered into a large tube placed within the tank and left until they acquired the tank temperature  $\theta_0$ ; they were then rapidly withdrawn and for the first time inverted—the air-bubble rising to the closed end. The case was opened for a moment and the dropper at once lowered into place by means of the



previously attached thread : this operation only occupied a couple of seconds. As the dropper left the case the latter was instantly closed by a second operator to prevent the escape of any benzene vapour left within it. Thus from the time of inversion no change took place in the temperature, and therefore in the volume of the air-bubble ; also no appreciable change in the temperature of the calorimeter ( $\theta_1$ ) was caused by the introduction of the dropper and contents. However, the mere act of opening the tube leading down to the calorimeter caused a slight lowering of  $\theta_1$ , and in order to re-establish the equality between  $\theta_1$  and  $\theta_0$  before commencing an experiment, it was necessary to switch on, for a second or two, the current from the exterior coil in the tank to the calorimeter coil. When the observer at the differential-thermometer galvanometer announced that  $\theta_0 - \theta_1$  was small and steady, the time for commencing the experiment had arrived.

10. In our later experiments, when we had become more expert at the various operations, the time from the insertion of the dropper to the commencement of an experiment was from 3 to 5 minutes. In our earlier observations at  $30^\circ$  the time was, however, much longer—from about 8 to 15 minutes. During this interval there was generally apparent a slight lowering of  $\theta_1$ , which made us fear that the evaporation through the capillary was appreciable, and it was not until our tenth experiment that a means of meeting this difficulty suggested itself. It was evidently necessary to wait until  $\theta_1$  became steady before commencing an experiment, and it was difficult to see how to shorten the time required to establish this condition.

From Experiment X. onwards the procedure was as follows. A glass rod whose upper end passed through a cork fitting the opening of the entrance-tube was lowered into the calorimeter. Round the lower three inches of this rod was strapped (by fine platinum wire) a thin roll of cotton-wool of which the upper two inches were saturated with benzene while the lower end was left dry, so that there was no danger of drops of benzene falling from it into the silver evaporating-flask.

The rod was withdrawn occasionally and more benzene added if the upper portion of the roll had become dry. Observation of the galvanometer showed when the cooling effect caused by the evaporation had ceased, and we were thus able to determine when the flask and connecting tubes were saturated. The rod was not finally withdrawn until the dropper was introduced : thus the space being saturated, no further evaporation took place ; and we believe that from Experiment X. onwards any error arising from evaporation in the time preceding the experiment may be disregarded.

After we had completed our experiments, we made some observations with the object of ascertaining the probable magnitude of the error in Experiments I. to VII. due to evaporation when the flask had not been previously saturated. A dropper was placed within the evaporating flask for 20 minutes and kept at a temperature of  $30^{\circ}\text{C}$ . It was then withdrawn, and the loss determined. As might have been expected, it varied slightly according to the droppers used, probably owing to the different sizes of the capillary opening.

In 20 minutes, dropper	II.	lost 10 milligrams,
"	"	III. " 12 "
"	"	IV. " 13 "

After Experiment VII. we adopted the plan of noting the time from the insertion of the dropper to the commencement of the experiment, but unfortunately we had not previously done so. We consider that the average time in these experiments must have been from 10 to 15 minutes ; the loss during this time would therefore appear to have been about 6 milligrams, or rather more than  $\frac{M}{1000}$ . Thus the values of L resulting from Experiments I. to VII. are probably too low by about 0.12. Fortunately we have six independent experiments at  $30^{\circ}\text{C}$ . (Nos. XXIX. to XXXIV.) in which this cause of error was absent.

We have entered into this matter fully, as it shows the importance of extreme attention to details in work of this kind, and also it was necessary to explain why we practically neglected Experiments I. to VII. when drawing our final conclusions. The same cause of error would slightly affect

Experiments VIII. and IX. at 40° C. At this time, however, we were attempting to minimize the evil by allowing as short a time as possible to elapse between the introduction of the dropper and the commencement of an experiment. We have also a note of the time, which in both cases was less than 4 minutes. The loss during this interval would probably not have affected the resulting values of  $L$  by more than .05, and we therefore do not consider it necessary to reject these experiments.

At the close of an experiment, when observation of the galvanometer showed that all evaporation had ceased, the dropper was extracted by means of a bent wire, immediately placed in its case, and weighed again after standing some hours in the balance-case.

Let  $m_1$  and  $m_2$  be the weights of the case and dropper before and after an experiment; the temperature of the balance-case was usually about 20° C., the specific gravity of benzene at that temperature may be taken as 0.88, hence  $M$  (true mass corrected to vacuo)

$$= m_1 - m_2 + (m_1 - m_2) \times .0012.$$

11. Before commencing the experiments it was necessary to ascertain if any alteration had taken place in the values of the various constants and variables since their determination in 1894.

Thermometers II. and A were re-standardized and it was found that a "zero-point rise" had taken place, as is customary with mercury thermometers.

Thermometer No. II. had risen 0.4 mm. = 0°·02 C. since its standardization in August 1894.

Thermometer A had risen 1.4 mm. = 0°·06 (nearly) since its standardization in July 1893, which is about the normal rise of thermometers of this description.

The platinum thermometer (AB) was removed from the calorimeter, strapped to its corresponding thermometer (CD), and placed in the tank whose temperature was raised from 18° C. to 40° C. Observations at different temperatures showed a rise of 0.45 mm. in the null-point whose position is now given by the formula  $598.8 + .03\theta$  in place of  $598.35 +$

·03 $\theta$ . If, however, this change, which probably took place in the arms of the bridge rather than in the thermometers \*, had not been detected the resulting error would have been negligible, for a difference of ·45 mm. in the setting of the null-point is equivalent (at 40°) to a temperature difference of about ·0041° C., and the total loss or gain by radiation, &c., corresponding to this difference between  $\theta_1$  and  $\theta_0$  would not exceed 0·2 thermal gram per half-hour, whereas the actual duration of the majority of these experiments was about 18 minutes.

The corrected formula was, however, used throughout these experiments for the adjustment of the contact-maker.

### 12. Value of $R_1$ .

The values of  $R_1$  were redetermined at temperatures 30°, 40°, and 50°. The corrected results showed falls of ·0012, ·0012, and ·0016 respectively from the values of 1894. These quantities have, therefore, to be subtracted from the values given in Paper W, table viii., but the correction is only 1 in 10,000 of  $R_1$ .

The following table gives the values of  $R_1$  used during the reductions of the observations on benzene.

(The suffix to  $R$  denotes the potential-difference in terms of a Clark cell.)

TABLE III.

Temp.	$R_{1c.}$	$R_{1c.}$	$R_{5c.}$
20	10·327	10·320	10·333
30	10·351	10·353	10·357
40	10·374	10·377	10·381
50	10·399	10·401	10·406

$$\delta R \text{ per } 1^\circ \text{ C.} = \cdot 0024.$$

The re-standardization of the Clark cells has already been referred to (section 6, p. 24).

\* [Note by E. H. G., August 12, 1895.—I have found by re-standardizing the bridge-arms, that the above supposition was correct.]

13.  $Q_s$ .

No alteration in the values of  $Q_s$  at  $30^\circ$  and  $40^\circ$  C. appears to have taken place.

The values of  $Q_s$  at  $50^\circ$  and  $20^\circ$  as given in Paper W, pp. 332, 333, appeared to have undergone alteration, and we therefore made a careful redetermination at those temperatures. The method adopted was that described on p. 292, Paper W, viz., the rate of rise in temperature at null-point was determined

(1) when the heat-supply was that due to the stirring only

$$= \left( \frac{d\theta_1}{dt} \right)_s, \text{ and}$$

(2) when the heat-supply was that due to the stirring and a potential-difference of 3 Clark cells

$$= \left( \frac{d\theta_1}{dt} \right)_{3\text{ces}}.$$

$$\text{Hence} \quad \frac{\left( \frac{d\theta_1}{dt} \right)_s}{\left( \frac{d\theta_1}{dt} \right)_{3\text{ces}} - \left( \frac{d\theta_1}{dt} \right)_s} \quad . \quad . \quad . \quad . \quad . \quad (A)$$

gives the ratio of the heat supplied by the stirring to the heat-supply when the potential-difference was that of 3 Clark cells; and as the latter can be calculated if  $R_1$  is known, the value of  $Q_s$  can be obtained without any assumptions as to the thermometric scale, the capacity for heat of the calorimeter, &c.

The individual experiments were in close agreement with each other and give the following results:—

At  $50^\circ$ ,  $\left( \frac{d\theta_1}{dt} \right)_{3\text{ces}} = .14533$  expressed in mm. of bridge-wire  
where rate of stirring =  $5.380$ ,

$$\left( \frac{d\theta_1}{dt} \right)_s = .001155, \text{ at rate } 5.380.$$

Hence  $Q_s$  (at rate  $5.380$ ) =  $.003404$ ;

but (see Paper W, p. 330)  $\frac{r^4}{Q_s} = \text{a constant} = \frac{837.8}{.003404}$ ,  
D 2

hence  $Q_s = \cdot 003206$  at rate 5·300.

A second determination gave

$$Q_s = \cdot 003202 \text{ at rate } 5\cdot 300.$$

A third gave

$$Q_s = \cdot 003205 \text{ at rate } 5\cdot 300.$$

We therefore assume

$$Q_s = \cdot 00321 + (r_1^4 - 789) \times \cdot 0000041,$$

as sufficiently accurate.

$$\text{At } 20^\circ, \left(\frac{d\theta_1}{dt}\right)_{3es} = \cdot 15941 \text{ at rate } 5\cdot 590,$$

$$\left(\frac{d\theta_1}{dt}\right)_s = \cdot 00427 \text{ at same rate.}$$

$$\text{Hence } Q_s \text{ (at rate } 5\cdot 590) = \cdot 01174 ;$$

$$\text{but } \frac{r_1^4}{Q_s} = \text{a constant} = \frac{976\cdot 6}{\cdot 01174},$$

$$\text{hence } Q_s = \cdot 00949 \text{ at rate } 5\cdot 300.$$

A second determination gave  $\cdot 00951$  at rate 5·300,

A third                   ,,                   ,,  $\cdot 00991$    ,,   ,, 5·300.

In this last experiment, however, there is internal evidence of some error in the time over the second interval. If we omit this interval and calculate the value of  $Q_s$  from the remaining intervals of that experiment, we get  $\cdot 00961$  as the value.

It is evident that  $\cdot 00950$  is a sufficiently close approximation.

We therefore assume

$$Q_s = \cdot 00950 + (r_1^4 - 789) \times \cdot 0000120.$$

Our experiments at  $30^\circ$  and  $40^\circ$  show that the values of  $Q_s$  at those temperatures as given in Paper W are correct. The errors at  $20^\circ$  and  $50^\circ$  as given in that paper were due to an arithmetical mistake, a difference having been added, instead of subtracted, in each case.

The following Table gives the expressions by which the value of  $Q_s$  can be obtained at any of the temperatures or rates given in succeeding Tables :—

TABLE IV.

Temp.	Value of $Q_s$ (in thermal grms.).
50	$\cdot 00321 + (t_1^4 - 789) \times \cdot 0000041$
40	$\cdot 00466 + (t_1^4 - 789) \times \cdot 0000059$
30	$\cdot 00665 + (t_1^4 - 789) \times \cdot 0000084$
20	$\cdot 00950 + (t_1^4 - 789) \times \cdot 0000120$

These changes in  $Q_s$  probably indicate the changes in the viscosity of the oil.

#### 14. *Alterations in the Apparatus.*

No alterations have been made except in exterior portions of the apparatus.

When working with water in 1894 there were, in the tubes leading to the air-pumps, one or two rubber joints which are now replaced by glass ones.

To prevent condensation, the benzene vapour after issuing from the tank passed over a row of small gas-jets and then down into a small Wolff's bottle, connected with the manometer and containing pumice-stone and sulphuric acid. It then passed through another tap\* into a large globe (capacity about 35 litres) also containing pumice-stone and sulphuric acid. By means of a water-pump the pressure in this globe was reduced to that of the aqueous vapour at the temperature of the tap-water. Its capacity was so great that the pressure in the Wolff's bottle could, at any time, be brought below that required, at experiments above  $20^\circ$ , by simply opening the tap communicating with the globe. Thus the water-pump had not to be used during an experiment, and, consequently, the two motors worked with greater regularity. The Wolff's bottle was also in direct communication with a Geissler's mercury-pump, by means of which, when working at the lower temperatures, the pressure was greatly reduced near the close of an experiment in order to secure the boiling-off of the last drop of benzene. We found that the mercury-

\* The grease on the core of taps traversed by benzene was replaced by phosphoric acid.

pump had to be kept in constant use during the experiments at  $20^{\circ}$ . With the exception of the above alterations and additions, the apparatus is the same in every respect as that figured in Plates 4, 5, and 6 of Paper W.

### 15. *On the Purity of the Benzene.*

The benzene, which was a sample of that used by Professor Ramsay and Miss Marshall for their comparative experiments, was supplied by Messrs. Kahlbaum of Berlin and guaranteed free from thiophene. It was redistilled twice from phosphoric anhydride, until it showed a perfectly constant boiling-point.

### 16. *Description of an Experiment.*

The dropper was placed in position (as described in section 9) and the contact-maker was then set, by means of a magnifying-glass, to the null-point corresponding to the tank temperature  $\theta_0$ .

When the observer (Observer II.) at the thermometer-galvanometer ( $G_2$ ) announced that  $\theta_1$  had become steady, three observations of the galvanometer-swing were taken, and the chronograph-key, being pressed at the second of those swings, recorded the time from which  $t_s$  was estimated. At the same moment Observer I. recorded the reading of thermometer II., which when reduced to the nitrogen scale gave the value of  $\theta_0'$ ,—the initial tank temperature.

As a rule the initial swings were somewhere between 0 and +50 (a swing of +50 would correspond to about  $+0.006^{\circ}$  C.), and, for reasons which will appear later, we preferred to have this initial swing (which gave the value of  $d'$ ) positive.

The Wolff's bottle (condenser A) had previously been exhausted down to the pressure of the large globe (condenser B) already referred to, but the tap between the two condensers had been closed. A tap (immersed in the tank-water) between the silver flask and condenser A was then opened, and the air expanding into A caused a fall in the manometer attached to it. The tap connecting condensers A and B was then gradually opened, and the pressure in the flask fell until some benzene was expelled from the dropper. The instant



this occurred the calorimeter temperature  $\theta_1$  commenced to fall, and Observer I. was acquainted with this fact by Observer II. who, throughout the whole experiment, was engaged in calling aloud the galvanometer-swings which resulted from the inversion of the battery connexions in the differential-thermometer circuit by means of a swinging key. The storage-cell current, which had been running for some time through a platinum-silver coil immersed in oil in the outer tank, was then switched on to the calorimeter-coil, the action recording itself on the chronograph-tape, and the potential balance then adjusted by means of the apparatus described in Paper J, p. 283. This balance had previously been approximately obtained while the current was running through the tank-coil; thus only a small additional adjustment was required and, as the temperature of the calorimeter-wire remained constant, the electrical balance required little attention, for the potential-difference rarely altered by as much

as  $\frac{E}{100,000}$  throughout an experiment. As the benzene vapour passed into condenser A the pressure in the flask increased, and thus the loss of heat by evaporation diminished. By a rapid movement of the tap between condensers A and B, the pressure could again be diminished and the cooling effect increased.

It was found impossible to control the rate of evaporation with the same perfection when using benzene as was the case in the experiments with water. The taps had to be constantly manipulated, and a moment's inattention on the part of Observer I. was immediately followed by a sudden rise or fall in  $\theta_1$ . This was more especially the case during the experiments at low temperatures. From about experiment V. or VI. onwards, however, the swings rarely amounted to as much as 200 or so, except during the first minute when the thermal balance was being obtained, at which time a swing of  $\pm 400$  or 500 was generally experienced. Throughout the whole of an experiment care was taken that any positive swing should be succeeded by a corresponding negative one. Although the announcement of swings of " + 200 " appeared alarming at the time, the extreme attention

devoted to the keeping down of these oscillations was really unnecessary. A swing of  $+200$  indicated that  $\theta_0$  was lower than  $\theta_1$  (at  $40^\circ$ ) by about  $0^\circ.02$  C., and the radiation &c. coefficient of the calorimeter being about  $.00009$  (in degrees per second per difference of  $1^\circ$ , Paper W, p. 289), this swing, even if maintained throughout the *whole time* that evaporation was proceeding (on an average less than about 7 minutes), would only have resulted in a *total* loss of about  $.00009 \times 318 \times .0216 \times 7 \times 60 = .25$  thermal gram \*. In no case, however, was a swing of such magnitude allowed to remain unaltered for more than a few seconds.

The chief difficulty was experienced near the close of an experiment. When working with water, there were always some indications that the end was near, for the pressure had to be diminished in order to maintain the thermal balance if only a drop or so remained. In the case of benzene, however, there were rarely any such indications; for the galvanometer-swing might be announced as  $+8$  or  $+10$ , and before the next announcement could be made it would be found that it had shot up to 300 or 400. After the preliminary experiment, it was of course possible to roughly estimate (knowing the weight of the dropper when filled) the probable duration of an experiment and, by adding it to the observed time of establishing the current, to predict approximately the time when evaporation would cease. Owing, however, to differences in the size of the air-bubbles necessarily left in the droppers, to the different rates of stirring, &c., and to errors in calculations made while all the attention of the observers was needed elsewhere, the current was very often switched off too late, thus increasing the value of the correction  $\Sigma g$  unnecessarily. If any mistake was made, the final value of  $\theta_1$  was in consequence higher than the initial one, for in those cases where the current was switched off too soon, it was always possible to bring  $\theta_1$  up to its initial value by re-establishing the current for a second or two; if, however,  $\theta_1$  was too high there was no means of diminishing it, all the benzene having been exhausted. Observer I. endeavoured, if possible,

\* About  $\frac{1}{2000}$  of the total "heat-supply."

to arrange so that the swing at the close of an experiment should be about  $-150$ , for the following reason. Evaporation having ceased and the current being switched off, the tap between the evaporating-flask and condenser A was closed, and a tap (also immersed in the tank-water) was slowly opened so that air (dried by having passed through sulphuric acid and phosphoric anhydride) was gradually admitted into the evaporating-flask through a 30 ft. copper coil immersed in the tank. Thus the air was at the temperature of the calorimeter. The heat liberated by its compression caused, however, a rise in  $\theta_1$  equivalent to a swing of about 120 ; thus no heat was, on the whole, gained by the calorimeter, for a corresponding loss had been experienced during the exhaustion. On this account we preferred to commence with a small positive swing, as it was not then necessary to reduce  $\theta_1$  so far at the close of an experiment to allow for this final increase. When Observer II. found that  $\theta_1$  had again become steady three final swings were taken, the chronograph-key being pressed at the middle one, thus giving the termination of the time  $t_s$  during which the stirring supply had to be estimated. Thermometer II. was read at the same time, and gave  $\theta''_0$ , the final tank temperature. Throughout the experiment, every thousand revolutions of the stirrer had been automatically recorded on the chronograph-tape.

The method of removing and weighing the empty dropper has already been indicated.

### 17. *Remarks on the Experiments.*

We give particulars of all our experiments with two exceptions. In No. XXI. *a.* the chronograph ceased to work during a critical portion of the experiment, and we were thus unable to determine  $t_E$ . In XXIV. *a.* Observer I. omitted to close the entrance tap to the evaporating-flask before connecting with the exhaust, thus the attempt to diminish the vacuum was a failure and the experiment was relinquished after a minute or so. In these two cases we at once performed other experiments to replace the failures, but retained the numbers for convenience of reference.

We have, however, rejected, when drawing our final con-

clusions, several of the experiments whose details are given. Such experiments are marked by a † in the Tables. We have, in no case, rejected any experiment *except as a consequence of some note made during that experiment*; that is, before reducing the observations we had already decided as to those which should be regarded as of little value. Thus we have in no way been guided by the results. For example, XXV. differs from the mean of its group by a greater quantity than either of the rejected experiments at that temperature: however, as we have no note against it, we are compelled to give it equal importance with any of the others. A simpler plan would have been to reject entirely the † experiments, but we think that a fairer idea of the general accuracy of the work is given by including all those that we completed.

The reasons for the rejection of the † experiments are given (as they appeared in our original notes) at the end of each group. We have, however, in each case given the mean of all in a footnote, and it will be seen that (except at 30°) our results would not have been appreciably affected by the inclusion of those rejected ones.

As a rule, we found that the thermal balance was most easily maintained when the potential-difference was that of 4 cells, but this supply of heat would have been somewhat too great at 20°, when we worked with 3 cells only. At all temperatures above 20° we performed experiments with 3, 4, and 5 cells, and we regard the agreement amongst the results as very satisfactory, and as establishing the validity of the various corrections. In thermal investigations it is as a rule difficult to alter all the conditions in so complete a manner as that caused by the changes above referred to. For example, if any "priming" had taken place (the usual cause of inaccuracy in determinations of the Latent Heat of Evaporation), its effect must have been greatly increased when the rate of evaporation was nearly trebled, which was the case when the potential-difference was altered from 3 to 5 cells. Again, the importance of the different terms undergoes such changes that any constant error in the determinations of  $Q_{st_s}$  and  $\Sigma q$  would cause the values of  $L$  when  $n=4$  to lie between the

values when  $n=3$  and  $n=5$ . An inspection of the Tables will show that no such effect is visible.

We also varied the "stirring supply" very considerably. The Tables show that (at the *same* temperature) the values of  $Q_s$  have been changed from .00276 (Expt. XVII.) to .00427 (Expt. XXIV.).

[*Note by E. H. GRIFFITHS.*—My experience with apparatus of a similar nature to that used in these experiments has convinced me of the severity of the test above referred to. During my attempts at a determination of the mechanical equivalent during the years 1887–1891 the results invariably broke down when thus tested. The following quotation, referring to the experiments anterior to 1892, is from p. 364, Paper J:—

"The agreement amongst individual experiments taken under the *same conditions*, was, if anything, at times more marked than in the experiments of 1892; nevertheless, when the final reduction took place, fatal discrepancies invariably showed themselves. . . . Experiments conducted with a high electromotive force invariably gave too great a value for the time as compared with that obtained when a lower electromotive force was used."

It appears to me that it is this power of altering all the conditions which renders electrical methods of such great value when applied to thermal determinations.]

### 18. *Explanation of the Tables.*

Tables lettered A give the experimental *data*; the deductions from those data are given in Tables lettered B.

(We have arranged the experiments in order of temperature rather than historical order, as consecutive experiments were not always at the same temperatures.)

#### TABLES A.

Col.	I. $a$ and $b$ give the number and date of the experiment.
„	II. $a$ and $b$ give the number of Clark cells in series, and the number of the dropper used.

- Col. III. gives the mass of benzene evaporated, after correction to *vacuo* (M).
- „ IV. The time during which the current was maintained ( $t_z$ ).
- „ V. The time from commencement to end of experiment ( $t_s$ ), *i. e.*, the time during which the “stirring supply” has to be estimated.
- „ VI. The number of revolutions per second ( $r_1$ ) of the stirrer.
- „ VII. The difference between the initial ( $\theta_0'$ ) and the final temperature ( $\theta_0''$ ) of the surrounding walls.
- „ VIII. Let  $\theta_1'$  (initial calorimeter temperature) exceed  $\theta_0'$  by  $d'$ , and let  $\theta_1''$  (final calorimeter temperature) exceed  $\theta_0''$  by  $d''$ ; then this column gives the value of  $d' - d''$ . Hence
- $$\{(\theta_0' - \theta_0'') - (d' - d'')\}$$
- gives the difference between the initial and final temperature of the calorimeter.
- „ IX. The capacity for heat of the calorimeter and its contents at the mean temperature of the tank ( $C_{\theta_1}$ ).
- „ X. The temperature of the Clark cells.
- „ XI. The value of  $R_{ne}$ , *i. e.*, the resistance of the calorimeter-coil at temperature  $\theta_1$ , when the potential-difference of its end is  $ne$ . (From Table III. p. 34.)

## 19. TABLES B.

(The numbers of the columns are similar to those in the corresponding tables of Paper W, where full particulars of the reductions are given.)

- Col. XV. The value of  $Q_z t_z = \frac{(ne)^2 \times t_z}{R_1 \times J}$ , where  $e$  is the potential-difference of 1 Clark cell, at the temperature given in Col. X. (*supra*). The values of  $R_1$  will be found in Table III. p. 34, and, as previously explained, the value of  $J = 4.199$  (see section 6, p. 24).

- Col. XVI. The value of  $Q_s$  deduced from Col. VI. by means of Table IV. p. 37.
- „ XVII. The value of  $Q_{stg}$ , the “stirring supply,” from Cols. V. and XIV.
- „ XVIII. The term  $\Sigma q = C_{\theta_1} \{(\theta_0' - \theta_0'') - (d' - d'')\}$  from Cols. VII., VIII., and IX.
- „ XIX. The sum of Cols. XV., XVII., and XVIII., that is, the total thermal grams ( $\Sigma$ ) required for the evaporation of M grms. of benzene.
- „ XX. The mean tank temperature ( $\theta_0$ ) of the experiment, expressed in the nitrogen scale.
- „ XXI. The value of  $L = \frac{\Sigma}{M}$ .

*Remarks on Experiments at 50°.*

Exp. XIX. *a.* “Mistake in switching off current, did not do so till  $\theta_1$  had risen so far that  $d''$  could not be obtained by means of galvanometer-swing. Had to readjust contact on bridge at close of experiment. Decided to regard experiment as a failure and repeat it.”

The experiment is included in the table to show that even the large resulting value of the term  $\Sigma q (-18.64)$  has but a small effect on the value of  $L$ , which differs from the mean at this temperature by less than 1 in 400. This value for  $L(98.90)$  should, however, certainly not influence our final conclusions.

Exp. XXIII.—“Mistake in connecting with vacuum, reduced pressure far below right amount, hence could not obtain proper thermal balance throughout experiment.”

*Conclusion.*

When  $\theta_0 = 50.014$ ,  $L = 99.14$ .

TABLE V.A.  
Experiments at 50° C.

I.	II.		III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
	a.	b.									
Number.	Date. July		M.	$t_E$ .	$t_S$ .	$\tau_1$ .	$\theta_0' - \theta_0''$ .	$d' - d''$ .	$O_{\theta_1}$ .	Temp. of Cells.	$R_{ac}$ .
	No. of Cells.	No. of Case.									
XVII.	4	II.	5.0339	658.4	1319.2	5.107	0°	-0.010	322	15.30	10.402
XVIII.	4	III.	4.7071	622.4	1118.7	5.118	0	-0.0154	"	15.30	"
+XIX. a.	4	IV.	4.9536	670.7	1204.3	5.126	-0.0020	-0.0560	"	15.30	"
XIX. b.	4	III.	4.7241	615.7	1093.2	5.241	+0.0025	+0.0046	"	15.64	"
XX.	4	V.	4.3654	569.1	997.0	5.171	+0.0054	-0.0030	"	15.21	"
XXI. b.	4	II.	4.9893	652.6	1314.9	5.219	+0.0005	-0.0030	"	15.70	"
XXII.	3	V.	4.3550	1010.1	1521.6	5.195	-0.0024	-0.0014	"	15.58	10.399
+XXIII.	5	IV.	4.9736	416.2	1024.2	5.411	+0.0024	-0.0047	"	15.77	10.406
XXIV. b.	5	IV.	5.0056	419.6	874.0	5.692	+0.0017	-0.0037	"	15.50	10.406
XXV.	3	V.	4.3899	1011.4	1405.4	5.653	+0.0054	-0.0068	"	15.50	10.399



TABLE V. B.  
Reduction of Experiments at 50° C.

I. a.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.
Number.	$Q_E t_E$ .	$Q_S$ .	$Q_{S/S}$ .	$\Sigma q$ .	$\Sigma$ .	$\theta_0$ .	L.
XVII.	496.00	.00276	3.64	- 0.32	499.32	49.993	99.20
XVIII.	468.85	.00279	3.12	- 4.97	467.00	49.984	99.20
+XIX. a.	505.21	.00280	3.28	- 18.64	489.95	49.983	98.90†
XIX. b.	463.55	.00307	3.35	+ 2.29	469.19	50.017	99.31
XX.	429.70	.00290	2.90	+ 0.78	433.37	50.026	99.27
XXI. b.	491.36	.00301	3.96	- 0.81	494.61	50.018	99.14
XXII.	427.93	.00296	4.50	- 1.22	431.21	50.027	99.02
+XXIII.	489.40	.00349	3.57	- 0.74	492.23	50.028	99.00†
XXIV. b.	493.52	.00427	3.74	- 1.29	495.97	50.021	99.08
XXV.	428.59	.00416	5.84	- 0.45	433.98	50.025	98.87
Mean (omitting those marked †) ..... If we include all experiments at this temperature we get ...							99.14 ± .034 99.10 ± .031

TABLE VI. A.  
Experiments at 40° C.

I.		II.		III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
a.	b.	No. of Cells.	b.	M.	$t_E$	$t_S$	$r_1$	$\theta_0' - \theta_0''$ .	$d' - d''$ .	$C_{q_1}$	Temp. of Cells.	$R_{ne}$
VIII.	8	4	III.	47228	628.2	1092.0	5.274	0	-0.049	318	16.27	10.377
IX.	9	4	IV.	50424	676.8	1155.0	5.220	+0.010	-0.192	"	15.90	"
X.	9	4	II.	50212	665.4	1169.3	5.171	-0.120	+0.023	"	15.70	"
+XI.	9	4	III.	47228	635.5	1074.6	5.176	-0.015	-0.0202	"	15.71	"
XII.	9	4	V.	43846	577.8	1105.3	5.118	-0.020	-0.016	"	15.72	"
XIII.	10	4	IV.	49994	670.2	1143.7	5.097	-0.145	-0.085	"	15.45	"
XIV.	10	4	II.	50258	662.0	1194.2	4.859	+0.030	+0.054	"	15.45	"
XV.	11	4	IV.	50051	668.6	1084.8	5.169	-0.051	-0.116	"	15.40	"
XVI.	11	4	II.	50286	678.3	1281.4	5.162	+0.051	-0.0430	"	15.50	"
XXVI.	19	3	V.	44191	1035.2	1471.5	5.242	-0.030	+0.027	"	15.32	10.374
XXVII.	19	5	III.	47469	406.0	779.8	5.237	+0.015	-0.118	"	15.32	10.381
XXVIII.	19	4	II.	50292	664.6	1066.6	5.238	+0.070	-0.070	"	15.34	10.377

TABLE VI. B.  
Reduction of Experiments at 40° C.

I. a.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.
Number.	$Q_e t_s$ .	$Q_s$ .	$Q_s t_s$ .	$\Sigma q$ .	$\Sigma$ .	$\rho_0$ .	L.
VIII.	473.86	.00437	4.99	- 1.56	477.29	39.965	101.04
IX.	510.68	.00439	5.07	- 5.79	509.96	40.090	101.12
X.	502.22	.00423	4.95	- 3.08	504.09	40.068	100.39
XXI.	479.49	.00424	4.56	- 7.12	476.93	40.078	100.99†
XII.	436.08	.00405	4.48	- 1.14	439.42	40.071	100.22
XIII.	505.96	.00399	4.16	- 7.31	502.81	40.055	100.57
XIV.	499.81	.00380	3.94	+ 2.67	506.42	40.065	100.76
XV.	504.79	.00422	4.58	- 5.31	504.06	40.058	100.70
XVI.	512.05	.00419	5.37	- 12.05	505.37	40.063	100.50
XXVI.	439.76	.00446	6.56	- 0.10	446.22	40.021	100.97
XXVII.	478.73	.00445	3.47	- 3.28	478.92	40.025	100.90
XXVIII.	501.77	.00445	4.75	0	506.32	40.025	100.70
Mean (omitting that marked †) .....							100.71 ± .057
If we include all experiments, we get .....							100.74 ± .054

TABLE VII.A.  
Experiments at 30° C.

I.		II.		III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	
a.	b.	Date, July	a.	b.	M.	$t_g$ .	$t_a$ .	$\tau_1$ .	$\theta_0' - \theta_0''$ .	$d' - d''$ .	$C_{\theta_1}$ .	Temp. of Cells.	$R_{ne}$ .
			No. of Cells.	No. of Case.									
† Prelim.	4		3	I.	3.5975	878.8	1617.0	5.691	0	-.0640	312	15.63	10.350
I.	5		4	III.	4.9107	661.6	1341.4	5.515	-.0108	-.0178	"	15.44	10.353
+ II.	5		4	IV.	5.0174	676.6	1210.9	5.177	-.0082	-.0212	"	15.59	"
III.	7		4	II.	5.1313	696.0	1102.3	5.473	0	-.0302	"	15.57	"
IV.	7		4	IV.	5.0071	674.7	1224.9	5.577	-.0088	-.0187	"	15.74	"
V.	7		4	V.	4.5336	607.9	1113.2	5.582	-.0096	-.0121	"	15.70	"
VI.	7		4	III.	4.8039	636.6	1144.5	5.120	+0.0103	-.0063	"	15.77	"
VII.	7		4	II.	5.2472	692.4	1251.5	5.091	+0.0061	+0.0088	"	15.89	"
XXIX.	22		3	V.	4.4083	1045.0	1438.8	5.238	-.0088	-.0085	"	14.85	10.351
XXX.	22		5	IV.	4.9873	431.1	939.5	5.252	+0.0031	-.0178	"	14.85	10.357
XXXI.	23		5	III.	4.7495	406.7	788.5	5.227	-.0077	+0.0037	"	14.82	10.357
XXXII.	23		3	V.	4.4459	1050.7	1434.8	5.156	0	-.0010	"	14.90	10.351
XXXIII.	23		5	II.	5.0477	437.8	840.9	5.227	-.0108	-.0068	"	14.78	10.357
XXXIV.	23		3	IV.	5.0226	1185.7	1645.3	5.241	0	-.0022	"	14.85	10.351

TABLE VII. B.  
Reduction of Experiments at 30° C.

I. a.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.
Number.	$Q_{\kappa} t_{\Sigma}$ .	$Q_s$ .	$Q_s t_{\Sigma}$ .	$\Sigma q$ .	$\Sigma$ .	$\theta_o$ .	L.
† Preliminary.							
I.	373.98	.00883	14.3	-19.96	368.32	29.820	102.36 †
† II.	500.60	.00779	10.45	- 8.92	502.13	29.990	102.25
III.	511.72	.00607	7.35	- 9.17	509.88	29.995	101.61 †
IV.	526.68	.00756	8.33	- 9.42	525.59	29.962	102.44
V.	510.41	.00815	9.98	- 8.38	511.81	30.000	102.24
VI.	459.90	.00818	9.11	- 6.77	462.24	29.971	101.97
VII.	481.59	.00580	6.64	+ 1.25	489.48	29.969	101.90
	523.62	.00567	7.10	+ 4.65	535.37	29.977	102.02
XXIX.	445.19	.00635	9.14	- 5.40	448.93	30.104	101.85
XXX.	509.70	.00641	6.02	- 4.59	511.13	30.117	102.46
XXXI.	480.95	.00629	4.96	- 1.25	484.66	30.034	102.05
XXXII.	447.50	.00596	8.55	- 0.31	455.74	30.047	102.50
XXXIII.	517.80	.00629	5.29	- 5.49	517.60	30.042	102.55
XXXIV.	504.26	.00636	10.46	- 0.69	514.03	30.052	102.34
Mean of Experiments XXIX. to XXXIV. ....							102.30 ± .076
† Mean of all (omitting Preliminary and II.) .....							102.22

*Remarks on Experiments at 40° C.*

Exp. XI.—“Reduced pressure far too much at commencement, was unable to obtain thermal balance until near end of experiment.”

Exp. VIII. & IX.—As pointed out (section 10, p. 33), the values of  $L$  are here probably in error by about 0.05. This, however, does not seem sufficient reason for rejecting them.

*Conclusion.*

When  $\theta_0 = 40.045$ ,  $L = 100.71$ .

*Remarks on Experiments at 30° C.*

Preliminary Exp.—The oscillations in  $\theta_1$  were very violent, as this was our first attempt at balancing when evaporating benzene; also, as we had no idea when to finish, the value of  $\Sigma q$  is very great. We have, however, inserted it to show how little such matters affect the result.

Exp. II.—“After inserting the dropper, had to withdraw it again owing to its sticking in the tube; dropper exposed for some time.” There is little doubt that, owing to the cooling when withdrawn, some air was sucked back, and hence there must have been some expulsion on re-introduction. We regret that we continued the experiment: the result is useless.

20. It will be noticed that the irregularities in this Table are greater than in preceding ones. These are due to two causes:—(1) The want of practice in the observers; (2) The value of the galvanometer-swings were not determined with sufficient accuracy until after Experiment VII., and, as the values of  $\Sigma q$  are large, any error might affect  $L$ , but probably not by more than  $\pm 0.1$ .

In Section 10, p. 32, we have given in full our reasons for considering that all these experiments (I. to VII.) are too low by about 0.12. The mean value of  $L$  given by them (omitting Preliminary and II.) is 102.14: thus it is probable that, had the flask been previously saturated with vapour, we should have obtained about 102.26, which is in fair agreement with the mean of the last six (102.30), where this cause of error

TABLE VIII. A.  
Experiments at 20° C.

I. a.	b.	II.		III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
		a.	b.									
		No. of Cells.	No. of Case.									
Number.	Date, July			M.	$t_E$ .	$t_S$ .	$\tau_1$ .	$\theta'_0 - \theta''_0$ .	$d' - d''$ .	$C_{\theta_1}$ .	Temp. of Cells.	$R_{ne}$ .
+ XXXV.	24	3	III.	47593	1129.6	1575.5	5.562	+0041	-0194	305	15.30	10.327
XXXVI.	24	3	IV.	50083	1182.1	1833.2	5.586	-0052	-0143	"	15.40	10.327

TABLE VIII. B.  
Reduction of Experiments at 20° C.

I. a.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.
	$Q_E t_E$ .	$Q_S$ .	$Q_E t_S$ .	$\Sigma q$ .	$\Sigma$ .	$\theta_0$ .	L.
+ XXXV.	482.02	-01151	18.14	-4.67	495.49	19.947	104.10 †
XXXVI.	504.42	-01172	21.48	-5.95	519.95	19.947	103.82

was non-existent. In any case, taking *all* the values as they stand in Col. XXI. (rejecting the † experiments), we get 102·22. The number 102·30, however, is the most probable value.

*Conclusion.*

When  $\theta_0 = 30\cdot066$ ,  $L = 102\cdot30$ .

*Remarks on Experiments at 20° C.*

Exp. XXXV.—This should be regarded as a preliminary experiment only. We had no idea of the pressure required to produce equilibrium, and had great difficulties in sufficiently reducing the pressure. “ $\theta_1$  was extremely irregular; the galvanometer-swing was often off the scale for a considerable period.”

Exp. XXXVI.—“This was a very fair experiment; the thermal balance well under control.”

We regret that we were unable to perform more experiments at 20° C. It was found necessary, however, to work the mercury-pump almost continuously, and this could not be done without further assistance\*. As such assistance was but rarely available, and as our time was drawing to a close, we were compelled to content ourselves with the above experiments.

*Conclusion.*

When  $\theta_0 = 19\cdot947$ ,  $L = 103\cdot82$ .

21. *Discussion of the Results.*

The values of  $L$  over the range 20° to 50° appear to be practically a linear function of the temperature.

If we assume

$$L = 107\cdot05 - 0\cdot1581 \theta, \quad . . . . (a)$$

we obtain a very close approximation to the experimental values, as shown by the following Table:—

\* We return our sincere thanks to Mr. C. T. Heycock, F.R.S., for his help during these experiments at 20° C.



TABLE IX.

Temperature. Nitrogen-scale.	L (expressed in terms of a thermal unit "at 15° C.").	
	By formula ( $\alpha$ ).	Experimental results.
50.014	99.14	99.14 $\pm$ .034
40.045	100.72	100.71 $\pm$ .057
30.066	102.30	102.30 $\pm$ .076
19.947	103.90	103.82

It is evident, therefore, that the curvature over the above temperature-range must be very slight.

The value of  $L$  cannot continue to be a linear function of  $\theta$  at very high temperatures, either in the case of benzene or water; for the critical point of benzene would fall at about 677° C., and that of water at about 990° C. It has, however, been shown that in the case of water the curvature from 0° to 100° (that is, over a pressure-range of about 4 mm. to 760 mm.) may be neglected (Paper W, pp. 316-321); and the above Table would indicate that we cannot be far wrong in making a similar assumption with regard to benzene, especially when we consider that both the temperature-range (0° to 80°·2 C.) and the pressure-range (26 mm. to 760 mm.) are in the latter case diminished.

We originally intended to perform a group of experiments at 60°, which is about the highest temperature to which it is advisable to expose the apparatus; but before doing so it would have been necessary to standardize a third mercury-thermometer—a work which would have occupied at least a week of the short time at our disposal.

Assuming formula ( $\alpha$ ) to hold to 760 mm., and taking the boiling-point at that pressure as 80°·20 C. (Ramsay and Young, Phil. Mag. 1887), we get

When  $\theta = 80.2$ ,  $L = 94.37$  ("thermal units at 15° C.").

The results of the experimental work described in this paper may be summarized as follows :—

The Latent Heat of Evaporation of Benzene over the temperature-range  $20^{\circ}$  to  $50^{\circ}$  C. (nitrogen-scale) is represented by the equation

$$L = 107.05 - 0.158 \theta,$$

where  $L$  is expressed in terms of a "thermal unit at  $15^{\circ}$  C."

Assuming this expression to hold over the range  $50^{\circ}$  to  $80^{\circ}$ , the resulting value of  $L$  at  $80^{\circ}.2$  C. (760 mm. pressure) is 94.37.

## 22. Historical.

We have been unable to find records of any determinations in addition to the following :—

REGNAULT. *Mémoires de l'Académie*, 1862, vol. xxvi. p. 761 :  
 $L = 109.0$ .

R. SCHIFF. Liebig's *Annalen*, 1886, vol. ccxxxiv. p. 338 :  
 $L = 93.4$  at  $80^{\circ}.35$ .

K. WIRTZ. Wiedemann's *Annalen*, 1890, vol. xl. p. 438 :  
 $L = 92.9$  at  $80^{\circ}.1$ .

JAHN. *Zeitschrift für Physikalische Chemie*, 1893, vol. xi. p. 79 :  
 $L = 107.6$ .

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