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On the Specific Heat of Steam at Atmospheric Pressure between 104 $ ^{\circ} $ C. and 115 $ ^{\circ} $ C.

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XIII. *On the Specific Heat of Steam at Atmospheric Pressure between 104° C. and 115° C.*

(*Experiments by the Continuous Flow Method of Calorimetry performed in the Physical Laboratory of the Royal College of Science, London.*)

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Preface.

The conclusion of Mr. Brinkworth's experiments on the specific heat of steam at atmospheric pressure in the neighbourhood of 105° C. marks a definite stage in an investigation which has been in progress with varying success for the last twenty years. It may therefore be of interest to review the situation in the light of collateral evidence which has been accumulating from various quarters during the progress of the research.

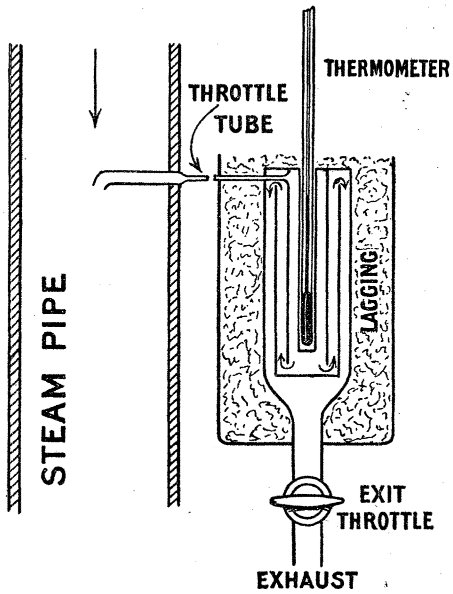

Fig. 1.

The investigation originated from some experiments undertaken in conjunction with the late Prof. J. T. Nicolson, at McGill College in 1895, "On the Law of Condensation of Steam" (published in 'Proc. Inst. C.E.,' 1898), in the course of which it was necessary to observe repeatedly the wetness of the steam employed. The special form of throttling calorimeter, shown diagrammatically in fig. 1, was employed for this purpose. The sample of steam, taken from the steam-pipe, was throttled through a thin tube of small bore, in order to eliminate the error due to conduction of heat through the throttle, to which most forms of throttling calorimeter then in vogue were liable.

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After circulating round the thermometer pocket, the throttled steam, before leaving the apparatus, was made to circulate twice round the calorimeter to minimise external loss. The whole apparatus, including the steam-pipe and the throttle tube, were also well lagged in the usual way. The pressure after passing the throttle was generally atmospheric, but an exit throttle and gauge were provided for raising the pressure and observing its value when required. The exit could also be connected, if desired, to a condenser vacuum.

The wetness of the steam $(1-q)$ was determined in the first instance by means of the usual formula with REGNAULT'S coefficients, namely,

$$(1-q)\,L' = 0{\cdot}305\,(t'-100)-0{\cdot}475\,(t''-100), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where L' is the latent heat of dry saturated steam at the initial temperature, t' and t'' is the temperature observed after throttling to atmospheric pressure. In spite of all precautions suggested by previous experience in calorimetry, the wetness of the steam persisted in coming out *negative* (which was obviously impossible) to an extent beyond the probable limits of error of observation. Since many at that time suspected REGNAULT'S value 0·475 of the specific heat, and had proposed other values, ranging from 0·380 (GRAY) to 0·568 (ZEUNER), it was decided to make a direct determination of the specific heat in the neighbourhood of 100° C. by the continuous electric method, which had been devised some years previously, for the determination of the mechanical equivalent of heat.

The first experiments on the specific heat by this method were made by passing a current of slightly superheated steam at atmospheric pressure over an electric heating coil, and observing the rise of temperature with a pile of several thermojunctions in series. The electric energy supplied was measured with standard Weston instruments, and the steam current by the usual method of condensation and weighing. This was a comparatively rough method, because the steam current could not be very accurately controlled, or the external loss exactly determined. Some difficulties were also experienced with the insulation of the thermojunctions. The results obtained showed discrepancies of 1 or 2 per cent., but indicated a value of the specific heat falling from 0·50 to 0·49 over the range of temperature from 110° C. to 160° C. covered by the experiments. This was regarded as a decisive confirmation of REGNAULT'S value 0·475 over the range 125° C. to 225° C., since a slight diminution of the specific heat with rise of temperature was to be expected owing to the existence of the Joule-Thomson cooling effect.

Having thus obtained by direct experiment the values of the mean specific heat at atmospheric pressure over the required range of temperature, it was possible to deduce the values of the total heat of saturated steam at temperatures above 100° C., from the observations already taken with the throttling calorimeter, by means of the equation,

$$H_s-H_{100} = S\,(t''-100) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where H_s is the total heat of the saturated steam at the initial temperature and pressure, and S is the mean specific heat at atmospheric pressure from 100° C. to t'', the temperature observed after throttling to atmospheric pressure. The curve of variation of total heat found in this way, instead of being straight like REGNAULT'S, with a constant coefficient $dH/dt = 0{\cdot}305$ for saturated steam, showed a decided curvature, the rate of increase falling from 0·40 calorie per 1° C. at 100° C. to 0·30 at 160° C. This indicated that REGNAULT'S coefficient 0·305 might be a fair average of the rate of variation over the range 100° C. to 200° C., where his experiments were most concordant, but that the coefficient probably increased at temperatures below 100° C., approximating to the value 0·475 (as it should according to RANKINE'S theory) at low pressures and temperatures, where the vapour should behave as a perfect gas. This view, while disagreeing materially with REGNAULT'S observations of the total heat at low temperatures, which were very discordant, gave good agreement with those of DIETERICI at 0° C., and of GRIFFITHS at 30° C. and 40° C. But in order to determine the complete variation of the total heat, H, from the thermodynamical formula

$$dH = S\,dT - SC\,dP, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and to deduce the form of the characteristic equation from the relation,

$$SC = T\,(dV/dT)_p - V, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

it was first necessary to determine more completely the variation of the cooling effect, C, over as wide a range of T and P as possible.

The Differential Throttling Calorimeter.

The single throttling calorimeter previously employed was well adapted for determining the variation of the total heat of saturated steam in terms of the specific heat at atmospheric pressure, but it was not well suited for obtaining values of the cooling effect, C, *at a particular point*. Values of C at a particular temperature and pressure could be obtained only by *successive* observations with the single calorimeter, during which the initial state of the steam might vary. Since a change of 1 per cent. in the wetness of the initial steam produced a change of about 10° C. in the observed temperature after throttling, it was most important to employ a *differential method* in which such effects were automatically eliminated. This was successfully accomplished by connecting two exactly similar calorimeters to the same steam supply, and adjusting the terminal pressures P′ and P″ by exit throttles to a suitable difference P′−P″ read on a differential gauge. The corresponding difference of temperature T′−T″ could be obtained by a single reading with a pair of differential platinum thermometers, from which the value of the cooling effect at the mean temperature and pressure, $C = (T'-T'')/(P'-P'')$, is directly obtained, with almost complete elimination of errors due to variation of wetness or external heat loss. The apparatus is shown diagrammatically in fig. 2. The calorimeters were made of very thin steel tube, and each was well lagged and drained, and doubly jacketed with its own exhaust, so that a steady state was reached within five minutes of turning on the steam. The throttle tubes were made interchangeable, so that the external loss could be determined by using throttles of different sizes simultaneously in the two calorimeters. The elimination of the heat-loss, in the usual method of employing the differential instrument with equal throttles, proved to be nearly perfect, but the observations were very useful in correcting the previous results with the single calorimeter. The apparatus was completed early in July, 1897, and was exhibited to several members of the British Association on the occasion of their visit to McGill College in August. But owing to pressure of other work the results could not be completed in time for the meeting at Toronto. About thirty observations were taken by Prof. Nicolson and myself during the vacation, which were supplemented by others taken by the Senior Demonstrator, Mr. H. M. Jaquays, and the fourth year students during the ensuing session. These confirmed the previous conclusions, but the work was unfortunately interrupted, before any observations had been obtained at temperatures above 180° C. or pressures above 130 lbs., by the unexpected translation of Prof. Nicolson and myself to posts in England early in 1898. Prof. Nicolson intended to set up a duplicate of the apparatus at Manchester as soon as possible, while I continued the investigation at University College. But facilities

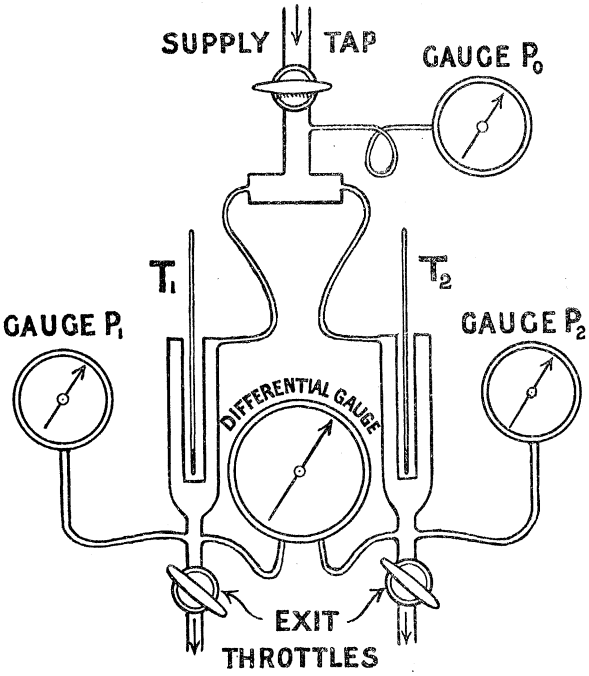

Fig. 2.

were lacking, and the necessity of fresh equipment caused inevitable delays. The experimental part of the work was still incomplete when the appearance of GRINDLEY's paper, "On the Cooling of Saturated Steam by Free Expansion" ('Phil Trans.' A, 1900) made it necessary to publish a preliminary account of the theory, which appeared in 'Roy. Soc. Proc.' for June, 1900.

GRINDLEY's observations of the cooling effect agreed remarkably well over the whole range with those given by the differential throttling calorimeter, although his experimental method was very different. But he deduced the values of the specific heat by assuming REGNAULT's formula $dH/dT = 0{\cdot}305$, for the rate of variation of the total heat of saturated steam, and obtained results for the specific heat at atmospheric pressure increasing from 0·387 at 100° C. to 0·665 at 160° C., which could not be reconciled with direct experiment. Owing to the uncertainty of REGNAULT's formula for the total heat, it seemed better to deduce the variation of the total heat from the measurements of the specific heat as already explained.

The theory of the relation between the total heat and the specific heat was worked out by assuming a modified form of the characteristic equation employed by RANKINE and by JOULE and THOMSON for a similar purpose. This equation was put in the form,

$$V-b = RT/P-c, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where b is the molecular volume of HIRN, a small constant of the same order of magnitude as the volume of the liquid, and c represents the diminution of volume of the vapour due to coaggregation or pairing of the molecules. JOULE and THOMSON deduced the values of c from their empirical expression $C = A/T^2$ for the cooling effect by integrating equation (4) on the assumption that S was constant. This method was shown to give unsatisfactory results in the case of CO_2, and was quite inadmissible in the case of steam. The opposite procedure was accordingly adopted; an expression AT^{-n} was assumed for c, and the resulting equation for SC, namely,

$$SC = (n+1)\,c-b, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

was compared with the experimental values obtained for S and C.

The complete variation of S with pressure was directly given by

$$S = S_0+n\,(n+1)\,cP/T, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where S_0 is a function of the temperature only, which appears from experiment to be very nearly constant over the experimental range for steam. The value of the index n was taken as being $S_0/R-1$, because it had been found by experiments with a sensitive platinum thermometer on the adiabatic compression of steam that the pressure temperature relation was of the form $P/T^{n+1} =$ constant, with n constant, which was shown to be thermodynamically exact in spite of variation of S, provided that $S_0/R = n+1$.

The numerical values for steam were deduced in the first instance with MAXWELL'S theoretical value 3·5 for the index n in the case of a triatomic molecule, because it happens, owing to the form of equation (6), that the value of n cannot be determined with great accuracy from observations on the cooling effect. The value $n = 3·5$ represented most of the properties of steam satisfactorily, including the saturation pressure, but did not agree very well with the observed values of the adiabatic index and the specific heat, which required a value of n more nearly approaching 3·3. This value was confirmed by experiments on the specific heat and the adiabatic index, which were then in progress, but could not be completed in time for inclusion in the original paper. The results of these experiments were first published in the article "Vaporisation," in the 'Encyclopædia Britannica,' 1902, where revised values for steam were given. The methods and apparatus employed were also described and exhibited at meetings of the Physical Society of London in October and November, 1902, but no detailed account of the work was published.

Continuous Flow Vacuum Calorimeter.

The principal improvements introduced in these experiments on the specific heat were as follows. The flow tube of the calorimeter, containing the heating coil and the thermometers, was enclosed in a vacuum jacket to minimise external heat-loss, which in turn was protected by an external steam jacket maintained at a pressure slightly above atmospheric. The electric energy was measured very accurately by means of a potentiometer and Weston cells, and the temperatures were observed with platinum thermometers in place of couples. The chief difficulty encountered at first was that of securing a perfectly steady temperature for the steam jacket, and a perfectly steady current of steam, which had not been obtainable in the earlier experiments in which steam had been taken from an ordinary boiler. This difficulty was finally overcome by employing a boiler heated by gas, the supply of which was regulated by the steam pressure itself acting on a mercury column. The regulator could be set to cut off at any desired pressure within certain limits, and worked with almost incredible perfection, maintaining the temperature in the jacket as nearly constant as the barometric fluctuations of pressure would permit. This regulator was subsequently employed by MAKOWER in experiments on the adiabatic index, and is fully described and illustrated by my collaborator in the following paper.

The method of obtaining a steady current of slightly superheated steam will be readily understood from the accompanying fig. 3, which illustrates one of the many arrangements adopted in measuring the specific heat.

The steam at a steady pressure from the regulator, after passing through the double-walled jacket surrounding the calorimeter, entered a separator at the top of the jacket where any entrained moisture was drained off. A glass tube of small bore fitted in the exit from the separator to the interior of the jacket, served as a throttle to determine the magnitude of the steam current, which could be varied in any desired ratio, within certain limits, by fitting throttles of different sizes. Apart from barometric variations, which were generally small, any desired current could be maintained constant to about 1 in 1000. After passing the throttle, the steam at atmospheric pressure, already slightly superheated, was raised very nearly to the temperature of the jacket by passing through a number of gauze discs. In the earlier experiments, the temperature of the steam on entering the vacuum jacket was taken by a platinum thermometer before reaching the heating coil. In many of the later experiments this thermometer was omitted, because the measurement was found to be superfluous, owing to the extreme steadiness of the regulator. The heating coil was of platinum, wound on a mica frame, having a resistance of about 5·5 ohms at 110° C. It was provided with current and potential leads, and connected in series with a 5-ohm manganin standard for measuring the current in the usual way. The leads to the heating coil were insulated by glass tubes (not shown) round which the steam, after passing the heating coil, was made to circulate spirally by a rubber coil or metal spiral nearly fitting the flow tube. The thermometers consisted of coils of silk-covered platinum wire, each having a fundamental interval of 1 ohm, and capable of sliding up or down in small bore tubes, 3·5 mm. diam., with the object of interchanging thermometers, and varying the immersion when desired. The bulbs were generally fixed at a distance of 10 cm. from the heating coil, to allow time for the mixing of the steam to a uniform temperature. The coils were wound on glass, and the copper leads were insulated by glass capillaries.

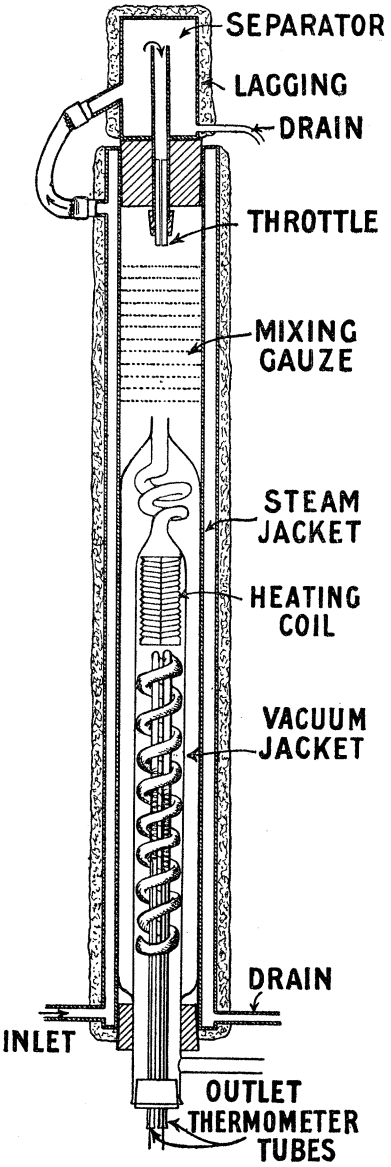

Fig. 3.

It would be tedious and unnecessary to describe in detail all the different arrangements adopted for measuring the specific heat, and the steps by which improvements were effected, but the following summary of observations taken with the apparatus above described, shortly after the reading of the paper on June 21st, 1900, is instructive as illustrating some of the difficulties of measurement in the immediate neighbourhood of the saturation point. The temperatures tabulated under θ', θ'' are the initial and final superheats reckoned from 100° C. The rise of temperature

$\theta''-\theta'$, denoted by $d\theta$ for brevity, is the observed change of temperature of the flow Q due to the supply of electric energy EC in watts. Q is given in grammes per second. The heat supplied per gramme per degree rise $EC/Qd\theta$ is the most convenient quantity to calculate in the first instance. The observed value has to be reduced, as subsequently explained, to allow for slight variations in the temperature limits θ' and θ''. The reduced values corresponding to the range 103° C. to 113° C. are denoted by X and are employed in calculating the results for S, h and k in the usual formula for the continuous-flow method, which may conveniently be expressed by the following equation :—

$$X = EC/Qd\theta = S+h/Q+k/Q^2.$$

The greater part of the heat-loss, represented by $hd\theta$ watts, appears to be independent of the flow and proportional to the rise $d\theta$, but there is usually a small term $kd\theta/Q$ varying inversely as the flow, due to conduction and other similar causes. X may be regarded as the uncorrected value of the specific heat, which always appears to increase with diminution of the flow, but tends to a limit coinciding with S as the flow is increased. From the values X_1, X_2, for any pair of flows Q_1, Q_2, reduced to the same range $d\theta$ if necessary, we obtain immediately by eliminating h,

$$S = (Q_1X_1-Q_2X_2)/(Q_1-Q_2)+k/Q_1Q_2 = S_{12}+k/Q_1Q_2,$$

where S_{12} is the value of S obtained by neglecting k as is often done. If three flows are available, designated by the suffixes 1, 2, 3, in descending order of magnitude, we may eliminate k by finding S_{23}, and obtain,

$$S = S_{12}+(S_{12}-S_{23})Q_3/(Q_1-Q_3) = (S_{12}Q_1-S_{23}Q_3)/(Q_1-Q_3).$$

The values of k and h are easily obtained from the relations,

$$k = Q_2Q_3(S-S_{23}), \qquad h = (X_3-S)Q_3-k/Q_3,$$

in which the smaller flows are preferably employed as giving the largest differences.

It will be observed that the complete expression for the specific heat, S, as deduced from the values of X for three flows by the above method, may be put in the following symmetrical form,

$$S = X_1Q_1^2/(Q_1-Q_2)(Q_1-Q_3) + X_2Q_2^2/(Q_2-Q_3)(Q_2-Q_1)+X_3Q_3^2/(Q_3-Q_1)(Q_3-Q_2),$$

which is useful in estimating the effect of errors of observation. Thus if the flows Q_1, Q_2, Q_3, are in the ratio 4 : 2 : 1, the terms depending on X_1, X_2, X_3, are approximately in the ratio 8 : 6 : 1, which shows that the accurate determination of X_3 is much less important than that of X_1 or X_2. Further, since each product XQ is independent of Q, the effect of percentage errors in the measurement of the flows are in the same proportion as the corresponding X terms in the expression for S. Thus an error of

3 in 1000 in flow 1, 2, or 3, will produce an error in S of 8, 6, or 1 in 1000 respectively. The flows could generally be measured to 0·0001 gr./sec., so that the error due to any one flow could not in general exceed 1 in 1500 on the value of S, and would be much less for the smallest flow, which was the most difficult to measure.

Since the values of h and k depend on relatively small differences, the values of S, calculated by this method from each single set of three flows, are very susceptible to small accidental errors in X, due to slight variations in the conditions, especially with flows taken on different days. Much better agreement may be obtained by taking a large number of observations under identical conditions, and employing constant mean values of h and k in the reduction of the series. This method has been adopted with most satisfactory results by Mr. BRINKWORTH, but could not be applied to the observations given in the following table, because the conditions were varied widely from day to day. The number of observations taken with each calorimetric arrangement was insufficient to enable the variations of h and k to be interpreted with certainty at the time. But Mr. BRINKWORTH has since shown that the values of heat-loss observed in these experiments, when plotted according to his method in fig. 10, show a most remarkable agreement with the results of his analysis. This is a very severe test, because the maximum heat-loss is less than 4 per cent. and each individual result is plotted separately. The agreement is so close that it leaves little doubt of the substantial accuracy of the observations. The only difference is that, owing to the arrangement of the leads, the heat-loss in my apparatus was somewhat greater than in his under similar conditions.

SUMMARY of Observations with Vacuum Calorimeters.

Date and flow.	Temperatures.		Rise. $d\theta$.	Flow. Q.	Watts. EC.	EC/Q $d\theta$ = X.		Results. S, h, and k.
	θ'.	θ''.				Observed.	Reduced.	
Unsilvered jacket. D = 7 cm. between heater and thermometer.								
June 25								
(3)	4·030	17·257	13·227	0·1577	4·774	2·289	2·309	S = 2·062
(2)	3·826	10·228	6·402	0·3302	4·513	2·135	2·135	h = 0·0110
(2)	3·831	13·121	9·290	0·3288	6·495	2·126	2·136	k = 0·0044
(1)	3·432	12·472	9·040	0·6072	11·467	2·088	2·092	
(1)	3·434	12·494	9·060	0·6067	11·462			
Silvered jacket. D = 7 cm. between heater and thermometer.								
June 28								
(1)	3·382	12·544	9·162	0·6035	11·463	2·073	2·077	S = 2·052
(2)	3·803	13·083	9·280	0·3304	6·450	2·104	2·114	h = 0·0085
(3)	4·012	13·599	9·587	0·1566	3·387	2·256	2·269	k = 0·0040

SUMMARY of Observations with Vacuum Calorimeters (continued).

Date and flow.	Temperatures.		Rise. $d\theta$.	Flow. Q.	Watts. EC.	EC/Q $d\theta$ = X.		Results. S, h, and k.
	θ'.	θ''.				Observed.	Reduced.	
New thermometers and heating coil, refitted to reduce k. D = 7·5 cm.								
July 9								
(2)	3·902	13·278	9·376	0·3427	6·378	1·985	—	Gauze only, no spiral.
(1)	3·551	12·516	8·965	0·6328	11·281	1·988	—	Insufficient mixing.
New silvered jacket. Mixing spiral refitted. D = 8 cm.								
July 10								
(1)	3·528	12·350	8·822	0·6200	11·401	2·084	2·089	S = 2·070
Pressure raised by altering regulator.								
(2)	4·703	12·566	7·863	0·3916	6·446	2·093	2·108	h = 0·0110
Pressure readjusted to previous value.								
(2)	3·749	13·119	9·370	0·3272	6·435	2·099	2·108	k = 0·0005
(3)	3·954	15·424	11·470	0·1568	3·856	2·144	2·160	
Repeated under slightly different conditions.								
July 12								
(3)	4·032	12·656	8·624	0·1566	2·906	2·152	2·163	S = 2·064
(1)	3·401	12·554	9·153	0·6042	11·532	2·085	2·089	h = 0·0137
July 13								
(1)	3·356	12·502	9·146	0·6043	11·515	2·083	2·086	k = 0·0003
(2)	3·712	13·045	9·333	0·3315	6·492	2·099	2·108	
Tin spiral in place of rubber for mixing. D = 8 cm.								
July 16								
(1)	3·376	13·226	9·850	0·5620	11·488	2·075	2·081	S_{12} = 2·068
(2)	3·800	14·307	9·707	0·3217	6·491	2·078	2·091	
(2)	3·800	11·320	6·720	0·3213	4·508	2·088	2·090	
(2)	3·800	8·877	4·277	0·3218	2·889	2·098	2·092	
(2)	3·800	6·991	2·391	0·3223	1·628	2·112	2·091	
Unsilvered jacket. Rubber mixing spiral. D = 9 cm.								
July 17								
(1)	3·343	12·102	8·759	0·6238	11·465	2·098	2·100	S_{12} = 2·072
(2)	3·777	12·930	9·153	0·3338	6·463	2·115	2·124	

SUMMARY of Observations with Vacuum Calorimeters (continued).

Date and flow.	Temperatures.		Rise. $d\theta$.	Flow. Q.	Watts. EC.	EC/Q $d\theta$ = X.		Results. S, h, and k.
	θ'.	θ''.				Observed.	Reduced.	
Same jacket. Single thermometer in place of pair. D = 9 cm.								
July 18								
(1)	3·357	12·101	8·744	0·6267	11·494	2·097	2·099	S = 2·063
(2)	3·796	12·962	9·166	0·3348	6·493	2·116	2·125	h = 0·0242
Lowered pressure by 2 cm.								
(3)	3·372	12·407	9·035	0·1478	2·897	2·170	2·173	k = −0·0012
Altered separator and fitted new condenser. D = 7·5 cm.								
July 19								
(3)	3·396	12·667	9·271	0·1452	2·896	2·152	2·156	S = 2·055
(1)	2·740	12·428	9·688	0·5710	11·533	2·085	2·079	h = 0·0132
(2)	3·178	13·168	9·990	0·3103	6·500	2·097	2·100	k = 0·0002
Rearranged leads of heater. D = 11 cm.								
July 24								
(1)	2·747	12·400	9·653	0·5543	11·437	2·139	2·133	S = 2·061
(2)	3·205	12·567	9·362	0·3163	6·460	2·183	2·184	h = 0·0413
(3)	3·400	11·812	8·412	0·1488	2·884	2·304	2·305	k = −0·00074
New silvered jacket. New rubber mixing spiral. D = 8·5 cm.								
July 28								
(3)	3·845	12·917	9·072	0·1451	2·943	2·236	2·246	S = 2·064
(2)	3·535	14·524	10·989	0·2794	6·575	2·142	2·153	h = 0·0230
(1)	3·214	16·174	12·960	0·4255	11·636	2·110	2·121	k = 0·0005
Same distance. Test for variation with range of temperature.								
July 30								
(1)	3·207	16·242	13·035	0·4223	11·590	2·105	2·116	
(1)	3·262	13·154	9·892	0·4243	8·869	2·113	2·117	
Altered distance to D = 6 cm.								
(1)	3·337	13·509	10·172	0·4240	8·857	2·054	2·060	S = 2·054
(2)	3·667	14·721	11·054	0·2842	6·487	2·065	2·077	h = −0·0046
(2)	3·665	8·604	4·939	0·2846	2·931	2·085	2·075	k = +0·0032
(3)	3·890	13·076	9·186	0·1455	2·890	2·162	2·172	

SUMMARY of Observations with Vacuum Calorimeters (continued).

Date and flow.	Temperatures.		Rise. $d\theta$.	Flow. Q.	Watts EC.	$EC/Q\,d\theta = X$.		Results. S, h, and k.
	θ'.	θ''.				Observed.	Reduced.	
	Altered distance to D = 10 cm. Same conditions.							
July 31								
(3)	3·812	12·687	8·875	0·1437	2·915	2·286	2·295	$S = 2\cdot060$
(1)	3·107	12·813	9·706	0·4287	8·889	2·136	2·137	$h = 0\cdot0327$
(2)	3·527	13·015	9·488	0·2840	5·847	2·170	2·177	$k = 0\cdot0001$
	Mean S = 2·060, 103° C. to 113° C.							

The value found for h increases, as one would naturally expect, when the distance between the heating coil and thermometer is increased. Conversely h may be diminished by reducing the distance, but it is necessary to allow sufficient space for the mixing of the steam to a uniform temperature, and it was found that D could not be reduced below 6 cm., even with the most effective spiral mixing of the flow. Mixing the fluid by passage through wire gauze, which has been commonly employed by other observers, was found to be very ineffective as compared with the turbulent flow induced by the spiral. The maximum value of h observed at a distance D = 11 cm. was only 3·5 per cent. of the heat supply for the largest flow. The average was about 2 per cent., but none of the jackets maintained a good vacuum when heated in steam, and they all cracked after a few days use. The term k/Q^2 was generally less than 1 in 1000 for the large flow, but increased to nearly 1 per cent. when the distance was reduced to 6 cm.

Since the measurement of the electric energy is made in watts, it is convenient to calculate X and S in joules or watt-seconds per gr. degree. The values of X are always a little greater than 2 for steam, and since the formulæ involve only differences between corresponding values of S and X, it saves a good deal of trouble in calculation to work only the differences from the round value 2000 in each case. It is important for the same reason to keep the differences between the flows as large as possible. The observed values of X_1 were generally consistent to 1 in 2000 or better, but an error of 1 in 2000 in the value of X_1 or X_2 would make an error of 3 or 2 in 2000 in the result calculated from 3 flows. The order of agreement of the results, which range from 2·052 to 2·070 is, therefore, as good as can be expected, considering the range of variation of the conditions of the experiments.

The results of this particular series of observations were reduced in the first instance by employing the theoretical formula (7) for the variation of the specific heat over different ranges. The mean result found in this way was S = 2·074, corresponding to S = 0·496 calories per 1° C., which agreed as closely as could be expected with my previous experiments by other methods, giving S = 0·497 over the same range. A systematic variation depending on the initial temperature was subsequently noticed, which requires further explanation, and which formed the starting point of fresh investigations.

Effect of Impurities in the Steam.

Steam in the immediate neighbourhood of the saturation point is liable to carry small particles of water in suspension, which cannot be evaporated completely by a moderate degree of superheat if any impurities, such as salt in solution, are present. Since 1 mgr. of water requires more than half a calorie to evaporate it, and the heat required to raise the temperature of 1 gr. of steam 10° C. is only 5 calories, it is necessary that the initial steam should not contain more than 1 in 100,000 of water, if the specific heat is to be found correct to 1 in 1000 over a range of 10° C.

The rise of boiling point θ produced by x gram-molecules of salt per gram of water is approximately $1000x$ ° C. The proportion of suspended water remaining unevaporated at any degree of superheat θ' will be $1000x/\theta'$. The quantity evaporated in heating the steam from θ' to θ'' will be $1000x(\theta''-\theta')/\theta'\theta''$. This will produce an apparent increase of the mean specific heat of the steam over the range $\theta''-\theta'$ equivalent to $1000\mathrm{L}x/\theta'\theta''$, where L is the latent heat of evaporation. It was found that this extremely simple and convenient reduction formula fitted the results obtained over different ranges of temperature with extraordinary precision, and reconciled apparent discrepancies which had previously been attributed to errors of observation. A few examples of this reduction are given in the preceding table, *e.g.*, the observations with flow (2) for different ranges of temperature on July 16th, which are seen to agree extremely well when reduced to a common range 103° C. to 113° C. by this formula. The numerical value of the constant $1000\mathrm{L}x$ in the reduction formula was found to be 1·73 joules, which would be equivalent to the presence in the steam of an impurity of about half a millionth of a gram-molecule of salt per gram. It is quite possible that an impurity of this order of magnitude might have been produced by the continued use of ordinary water in the boiler, and the passage of the steam through considerable lengths of rubber and glass tubing. Small variations in the impurity might also account for some of the differences in the results obtained on different occasions, but as the same boiler and regulator were employed in all cases, the variations in the quality of the steam supplied would probably be unimportant.

The effect of this reduction is evidently greatest when the superheat is small. Any small change in the initial superheat θ' was found to produce a relatively large effect on the results. The length of the steam jacket cannot allow sufficient time for raising the steam exactly to the temperature of the jacket before entering the calorimeter. There is always a systematic fall of initial temperature with increase of flow, which is clearly shown in the table of observations. The application of this correction has accordingly the effect of reducing the mean value of the specific heat from the value S = 2·074, originally obtained, to 2·060 joules per gr. per 1° C., or from 0·496 calories to 0·493, over the range 103° C. to 113° C.

The value so obtained has still to be corrected for the water present in the steam, which was probably of the order of 2 parts in 10,000 at the initial temperature of 103° C. The correction can be obtained from the reduction formula, regarded simply as expressing the results of experiment, without requiring an exact knowledge of the nature of the impurity present. Assuming that the formula applies up to a temperature of 113° C., which was within the range of the experiments, and that all the water would probably be evaporated by the time the steam had reached this temperature, the value of the specific heat at 113° C. given by the formula of reduction, should be approximately that of dry steam at this temperature. If the correction to the *mean* specific heat over the range θ' to θ'' is given by the formula $1{\cdot}73/\theta'\,\theta''$, the correction to the specific heat *at* any temperature θ is given by $1{\cdot}73/\theta^2$. The value of the specific heat at 113° C. will be less than the mean over the range 103° C. to 113° C. by $1{\cdot}73/3\times 13 - 1{\cdot}73/13^2$, which is 0·0342 joules per 1° C. If the value from 103° C. to 113° C. is 2·060, the value *at* 113° C. will be 2·026 joules, which agrees very well with the value 2·030 at 105° C. obtained by my collaborator, when special precautions were taken to secure dry steam free from impurities. Briefly enumerated these precautions include (1) a higher initial temperature; (2) a much longer steam jacket; (3) pure water for the boiler; (4) tubes of pure tin in place of glass or rubber, for conveying the steam to the calorimeter; (5) special attention to the arrangement of the separator and drain tubes for removing water of condensation.

Indirect Verification.

The results obtained for steam with the apparatus above described were indirectly verified in various ways, so that there could be little doubt that they represented correctly the specific heat of the steam actually employed, although there might be a slight uncertainty as to the quality of the steam. The first method of verification applied was to use the same apparatus for finding the specific heat of air. There was in this case no difficulty with regard to wetness or insulation, and it was possible to employ thermometers of bare wire in addition to the tube thermometers. The results found for the specific heat of air at atmospheric pressure lay between 0·240 and 0·241 gr. calories per gr. per 1° C. and were about 2 per cent. larger than those given by REGNAULT, but agreed very well with the value deduced from JOLY's experiments at constant volume, and with the known value of the adiabatic index for air. The chief difficulty encountered was the regulation and measurement of the air current. This was overcome by constructing a delicately balanced and compensated gasometer for maintaining a steady pressure, and passing the air current through a resistance consisting of 20 small-bore tubes in parallel, immersed in a water bath to keep the temperature steady. The current was measured and adjusted by observing with an oil gauge the difference of pressure between the ends of the resistance. The same apparatus was subsequently employed by SWANN ('Phil. Trans.' A, 210, pp. 199–238, 1910) in a more accurate and extended investigation of the specific heats of air and CO_2. SWANN found the value 0·2414 for air at 0° C., which corroborated the conclusion that REGNAULT's value was appreciably too low.

A more direct verification of the result for steam was obtained by measuring the adiabatic index $n+1$ in the equation P/T^{n+1} = constant, at 108° C. in the neighbourhood of atmospheric pressure, by means of a compensated platinum thermometer of 0·001-in. wire, similar to those employed in the experiments with Prof. NICOLSON on the law of condensation of steam in 1895. The resulting values of the index lay between 4·26 and 4·30, giving, according to the foregoing theory, values of S at atmospheric pressure and 108° C. lying between 0·488 and 0·493 calories per gr. deg. These experiments were performed by W. MAKOWER at University College under my direction in 1901–2, and were published in the 'Phil. Mag.' for January, 1903.

Results of other Observers.

The experiments of HOLBORN and HENNING ('Ann. Phys.,' 18, p. 739, 1905), extending over the range 110° C. to 820° C. at atmospheric pressure, indicated that the specific heat of steam was constant within the limits of error of their observations, but threw no light on the variation with pressure in the neighbourhood of saturation, as their lowest range extended from 110° C. to 270° C. Their results gave most accurately the *ratio* of the specific heat of steam to that of air, which was found to be 1·940 over their lowest range. Their value for air being 0·2315 over the same range, that for steam would be 0·449, which is evidently too low, on account of the error of the value 0·2315 for air. SWANN's value (*loc. cit.*) for air over this range, namely, 0·2443,* with the same ratio 1·940, would give the value 0·474 for steam, agreeing closely with REGNAULT's value from 125° C. to 225° C. If equation (7) is adopted for the variation of the specific heat, this result would correspond to a value 0·482 for the specific heat at 108° C. and 1 atmosphere. The agreement with the value 0·485 found for dry steam at 108° C. is fairly close, but rests on the assumption that the specific heat at zero pressure is accurately constant, which may be to some extent in error. The results of explosion experiments indicate a considerable increase in the specific heat at high temperatures, which, if represented by a linear formula, according to the common practice, would require an increase 0·00034 in the specific heat per 1° C., or 0·027 between 110° C. and 190° C., which is more than sufficient to compensate for the diminution 0·008 over this range represented by the term

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* This value has quite recently been confirmed by HOLBORN and HENNING.

$n(n+1)c\text{P}/\text{T}$ in equation (7). It is probable that the variation of S_0 with temperatur is not linear, but is more rapid at high temperatures, as indicated by the radiation theory of the variation of specific heat suggested in the Report of the B.A. Committee on Gaseous Explosions (B.A. Rep., 1908, p. 340). At the same time there is probably an appreciable increase over the range 100° C. to 200° C., since the equation of saturation pressure appears to require a mean value of $S_0 = 0{\cdot}477$ over this range, but a lower value from 0° C. to 100° C.

The observations of KNOBLAUCH and JACOB ('Forsch. Ver. Deut. Ing.,' 35, p. 109, 1906) extending from 2 to 8 kg./cm^2 and from 150° C. to 350° C., showed a variation of S *with pressure* of the same type as that indicated by equation (7). The absolute value of the change with pressure found by these observers agreed with that given by formula (7) at a temperature of 210° C., but increased more rapidly below this point, and diminished more rapidly at higher temperatures. On the other hand, the value of the specific heat S_0 at zero pressure, obtained by extrapolation, showed an increase from 0·447 at 100° C. to 509 at 400° C., giving nearly the same rate of variation between these limits as that found by LANGEN in his explosion experiments at much higher temperatures. This variation could not possibly be reconciled with the experiments of HOLBORN and HENNING. A repetition of the observations by KNOBLAUCH and H. MOLLIER ('Zeit. Ver. Deut. Ing.,' 1911, p. 665), raised the results at 120° C. by 0·026, and lowered the results at 400° C. by 0·020, reducing the increase with temperature over this range from 0·062 to 0·016, which is quite a possible value. The magnitude of the correction, amounting to 10 per cent. on the specific heat, illustrates the difficulty of determining the variation of the specific heat by the methods which they described, since the variation is of the same order as the systematic errors of experiment. This correction brings the results of KNOBLAUCH and MOLLIER into very fair agreement with those given by equation (7), except that their results for the variation with pressure near the saturation line, obtained chiefly by extrapolation, appear to be excessive, and cannot be reconciled with experiments on the cooling effect.

Although it is probable that there is some variation of S_0 with temperature, the amount of the variation is so small and uncertain over the range required in steam-engine practice that it seems best for the present to take a mean value of S_0 in equation (7) for practical purposes. It is almost certain that the variation of S_0 cannot be linear. No exact theory of the variation has yet been proposed, and any attempt to represent it by an empirical formula would be highly speculative, and would introduce endless complications in the theory, without offering any material advantages so far as the steam-engine is concerned. The mean value of S_0 adopted in 1902 as giving the best general agreement over the required range was 13R/3 or 0·478. The present investigation appears to show that the actual value of S_0 at 100° C. is 0·463, but since it is very difficult to obtain perfectly dry steam near saturation (especially in the throttling experiments), and since S_0 probably increases with temperature, it appears likely that a constant mean value, such as 0·477, over the range 100° C. to 300° C., will agree better than a variable value with actua practice, in addition to simplifying the theory.

Later Experiments.

The differential throttling calorimeter was redesigned for higher pressures and temperatures in conjunction with Prof. DALBY in 1906, and was set up in the laboratory of the City and Guilds Institution (now part of the Imperial College of Science), at South Kensington. The late Prof. ASHCROFT assisted the writer in taking a series of observations on superheated steam. A differential platinum thermometer was employed for reading the temperature difference, and a mercury gauge for the pressure difference. The observations extended to an upper limit of 376° C. and agreed so closely with the variation of the cooling effect predicted by equations (6) and (7), that it was not considered worth while to publish them in detail, as it was hoped to obtain a more complete series at much higher pressures as soon as a suitable boiler and regulator could be installed. Owing to the great increase in the number of students in the engineering department, which necessitated a continual rearrangement of laboratories and equipment, it was found to be impossible to proceed with this work at the time. But the opening of the new engineering building is expected to relieve the pressure, and permit the work to be resumed at an early date. The apparatus is designed for simultaneous measurements of S and C under the same conditions, which is particularly advantageous, since both are required in the equations.

About the same time, preparations were made for attacking the problem of the variation of specific heat with temperature from the theoretical side, by a quantitative investigation of the absorption and emission spectra of gases in the infra red, which must, according to the theory of radiation, be intimately related to the variation of the specific heat. The elaborate apparatus required for this purpose was made in the physics workshop of the Imperial College, and took some years to construct, in consequence of the great pressure of other work. It was practically completed two years ago, and gave promise of supplying very useful information, but the work has now been brought to a standstill for want of funds to supply the necessary assistance and materials for carrying it on. It is hoped that something may be done towards the solution of this important problem when the assistants now serving at the front are set free at the conclusion of the war, but the work requires two or more observers, and nothing can be done without highly trained assistants, owing to the great difficulty and delicacy of the observations.

H. L. C.

On the Specific Heat of Steam at Atmospheric Pressure between 104° C. and 115° C.

By J. H. Brinkworth, *A.R.C.S.*, *B.Sc.*, *Lecturer in Physics at St. Thomas's Hospital Medical School.*

Introduction.

With one exception, all the experimental determinations of the specific heat of steam at atmospheric pressure have been made with steam considerably superheated. The first reliable investigations were made by Regnault, and the value he obtained, when corrected for various errors, reduces to 0·475; this being the mean specific heat over the range 125° C. to 225° C. Prof. Callendar, using the continuous flow method of calorimetry, has made the one determination previously quoted, in which the specific heat at atmospheric pressure was measured at a temperature not far removed from that of saturation. The value experimentally obtained, 0·493 over the range 103° C. to 113° C., is somewhat higher than that deduced by extrapolation from the results of other observers, and requires reduction (as above explained, p. 396) in order to allow for a minute fraction (about 1 in 10,000) of water present in the steam. In consequence, Prof. Callendar suggested to me that a redetermination of the specific heat of steam near 100° C. was desirable. My other duties are such as to allow only a certain amount of time for research, hence this investigation has been rather protracted; but through the whole course of the work I have been encouraged by Prof. Callendar, and here I wish to record my great indebtedness for the advice he has always given so readily. This investigation has been carried out in the Physical Laboratories of the Imperial College of Science, and I desire to acknowledge the kindness of the Board of Governors in furnishing me with the necessary equipment and with laboratory accommodation for so long a period.

Outline of the Method.

Steam is generated in a boiler of about 15 litres capacity and thence led to one limb of a U-tube pressure regulator, to be described in detail later. The pressure of the steam forces the mercury down in this limb of the U-tube and up in the other limb in which the adjustment of the supply of gas to the large ring burner, used for heating the water in the boiler, is made. After passing the regulator, the steam, now maintained at a constant pressure, is led between the walls of a jacket surrounding the calorimeter proper, thence through a separator and a throttle into the space enclosed by the double-walled jacket, whence it passes down the calorimeter flow-tube to a condenser. During the passage of the steam through the flow-tube it is heated by means of an electric current passing through a platinum heating coil, and its temperature is measured on a platinum resistance thermometer. Another temperature measurement is made when the supply of electrical energy is cut off, and the difference between these two temperatures gives the rise in temperature $d\theta$ of the steam. If C_1 is the electric current and E_1 the potential difference between the ends of the heating coil, we have, when the temperature conditions through the apparatus are steady,

$$C_1E_1 = SQ_1\,d\theta + h_1 d\theta,$$

where $h_1 d\theta$ is a term representing the heat-loss, and S is measured in joules per gr. degree C. If now, in similar experiments, the rates of flow, Q, of the steam are about one-half and one-quarter of the above value respectively, and if the electric current is adjusted in each experiment so that the rise in temperature of the steam is the same as before, we have

$$C_2E_2 = SQ_2 d\theta + h_1 d\theta$$

and

$$C_3E_3 = SQ_3 d\theta + h_1 d\theta.$$

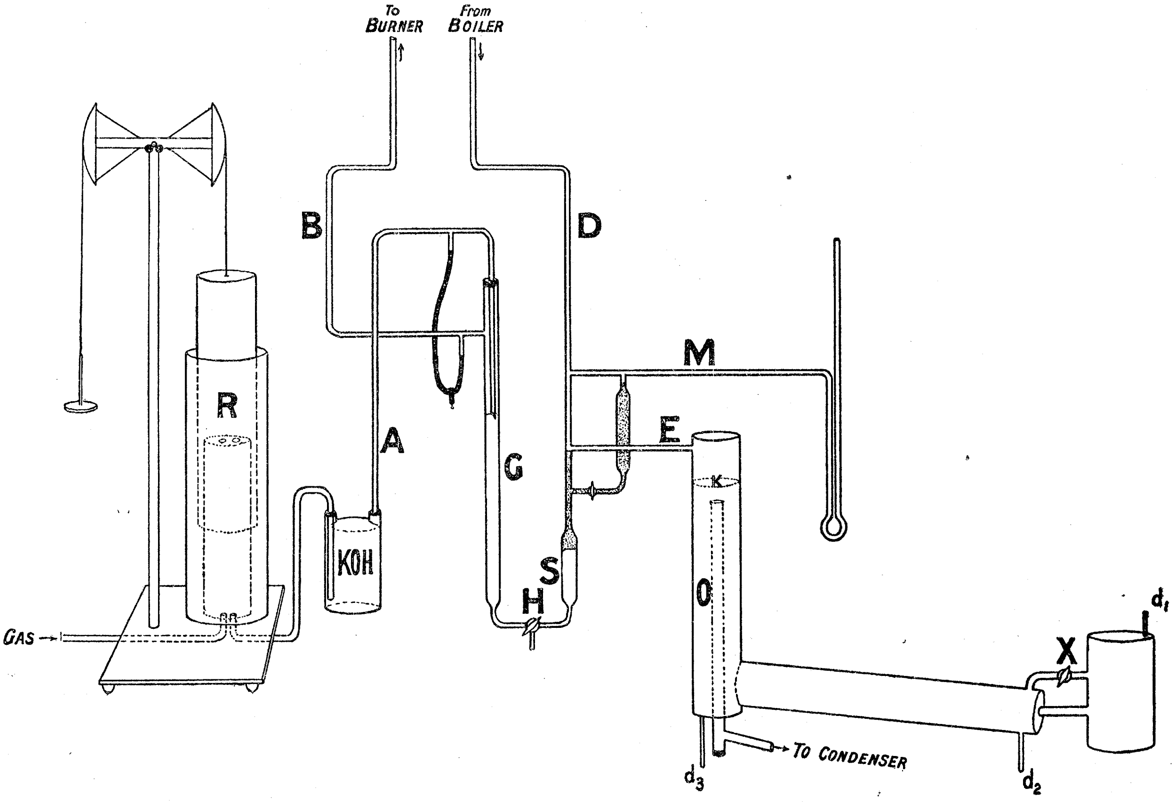

Fig. 4.

If the heat-loss is independent of the flow, a linear relationship will exist between the values of $CE/Qd\theta$ and the corresponding values of $1/Q$, but if this is not so, another term depending on the flow must be inserted in the fundamental equation, which then becomes

$$CE = SQd\theta + (h + k/Q)\,d\theta.$$

By means of three equations of this form we can obtain the values of S, h, and k.

The arrangement of the apparatus is represented diagrammatically in fig. 4. The gas, supplied from the mains, was led into the gas holder, R, from which it passed through a Wolff's bottle containing sticks of KOH, into the limb, G, of the pressure regulator and thence through the tube, B, to the burner. The steam generated in the boiler was led through block tin tubes to the other limb, DS, of the regulator, thence through E into the calorimetric apparatus and separator from which it passed down the flow-tube to the condenser.

Measurement of Electrical Energy.

An insulated battery of 60-ampere-hour accumulators supplied the steady current to the heating-coil through a standardised resistance of approximately the same value and a rheostat. The method adopted for connecting the heating-coil in the circuit is indicated in fig. 5. The four leads coming from the heating-coil are led into four mercury cups, and the main current leads are similarly led into two other cups cut in the same block of paraffin wax. With the aid of two copper connectors either pair of leads may be made the "current-leads" to and from the heating-coil, the other pair functioning as "potential-leads." By means of this arrangement it is also possible to send the current through either pair of leads connected to one end of the heating-coil and thus to investigate the heating effect due to the passage of the current through the leads. The potential differences across the heating-coil, across the standardised resistance and across a known number of cadmium cells in series, were obtained in terms of the readings on a Thomson-Varley 2-dial potentiometer. If X_1, X_2 and X_0 are the corresponding readings when the conditions are steady, the energy per second, in watts, supplied to the heating-coil and used in heating the steam, is

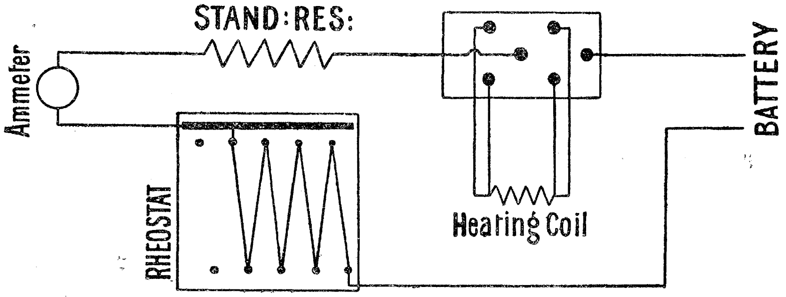

Fig. 5.

$$\mathrm{CE} = \frac{X_1 X_2 e^2 n^2}{X_0^2 R}.$$

Where

R = resistance of the standardised coil.

e = E.M.F. of a cadmium cell.

n = number of cadmium cells employed.

In order to maintain the same rise of temperature for different values of the steam flow, it was necessary to alter both the number of accumulators and the rheostat. With the flows used and for a rise of temperature of about 8° C., 9, 6 and 4 accumulators were required for the maximum, medium and minimum flows respectively; the final adjustment of the current, to give a constant value of $d\theta$, being made by means of the rheostat. This rheostat, which is also shown in fig. 5, consisted of pieces of manganin wire (No. 20) each about 35 cm. long. By means of the arrangement of mercury cups and the trough, indicated in the diagram, any number of these wires could be connected in series or in parallel until the requisite current was obtained.

The Standardised Resistance.

This consisted of a coil of No. 22 manganin wire wound on a wooden frame which was placed in oil contained in a double-walled vessel. A current of cold water was passed through the space between the double walls, and the temperature was taken by a mercury thermometer dipping into the oil; this temperature was assumed to be that of the coil itself. This secondary standard was compared with a 10-ohm primary standard. The same current was passed through both, and the potential differences across the ends of the resistances were obtained by the potentiometer. The results of several comparisons, full details of which have been kept, show that the resistance of the secondary standard is 5·0136 ohms at 17° C., and the temperature coefficient of resistance 0·000020.

The Cadmium Cells.

The cadmium cells used were of the **H**-pattern and were some of a set of twelve cells which I made in 1906, the instructions given by JAEGER and WACHSMUTH being accurately followed. The mercurous sulphate and cadmium sulphate were supplied by KAHLBAUM. Only seven of these cells have been used, Nos. 1 to 7 inclusive, in those experiments in which seven cells were required, and Nos. 2 to 6, or 3 to 6 for those experiments in which either five or four cells were required as a standard of electro-motive force. During the experiments the cells were immersed in an oil-bath, the current of water used for cooling the standardised resistance being first led round the nest of cells through a compo-tube immersed in the oil. Cell No. 7 was sent to the National Physical Laboratory to be tested in 1908, and again in 1913, and the two reports give the values 1·01875 volts at 17° C. in 1908 and 1·01860 volts at 17° C. in 1913. The N.P.L. comparisons were made with Weston normal cells, the E.M.F.'s of which have been directly determined in terms of the international ohm and the international ampere (10^{-1} C.G.S.), and found to be 1·0183 international volts at 20° C. During the 1913 standardisation the cell was put through a temperature cycle of 10° C., from 15° C. to 25° C., and though examined daily over a period of three weeks, no anomalous changes of E.M.F. with temperature were recorded. All the cells used in these experiments have been compared with No. 7 at various dates, and the differences between this cell and any individual cell have remained small and approximately constant. The differences expressed in hundredths of a milli-volt, between any cell and No. 7 are given in the following table, the negative sign indicating the amount to be subtracted from the E.M.F. of cell No. 7 in order to obtain the E.M.F. of the cell in question.

Date.	Temperature.	Number of cell.						
		1.	2.	3.	4.	5.	6.	7.
	° C.							
July 21, 1908 . . .	21	− 1	−17	− 5	−16	−2	0	standard at N.P.L.
September 22, 1908 .	17	− 1	− 8	− 1	−15	+1	standard	
August 2, 1910. . .	20	+10	0	− 4	−33	+8	+13	standard
May 5, 1913 . . .	17·5	+18	−18	−12	−24	+3	+21	,,
May 11, 1914 . . .	17	+22	−20	−10	−31	−2	+25	,,

From the last three sets of observations it will be seen that the cells used in these experiments have remained constant to 1 part in 10,000 over a period of nearly four years.

The Potentiometer.

This was of the well-known Thomson-Varley pattern with two dials, its total resistance being 100,000 ohms. The current for the potentiometer was supplied by Leclanché cells, the number employed being adjusted in accordance with the magnitude of the electric current in the main circuit, to make the potentiometer readings greater than 5000. The galvanometer used was of the Thomson pattern, having a resistance of 7000 ohms, and the sensitiveness was such that a change of unit amount on the vernier-dial of the potentiometer produced an alteration of 7 scale-divisions in the galvanometer deflection. A calibration of the potentiometer showed that no error amounting to 1 in 10,000 could be introduced by any arrangement of the sliders.

The Pressure Regulator (fig. 6).

This was of the form designed by Prof. CALLENDAR, and exhibited by him at a meeting of the Physical Society of London in 1902. It consists, essentially, of a U-tube the limbs of which, lettered G and S respectively, are partially filled with mercury. The gas after passing through a Wolff's bottle containing sticks of KOH, to remove impurities in the gas, is led into the limb, G, through a tube, A, the lower end of which is ground so that its cross-section is elliptical. The gas then passes out through B to the burner. In the tubes, A and B, there are T-connections which are joined by a rubber tube, C, on which is a screw-down stop-cock, whereby the amount of gas going through this bye-pass can be adjusted.

Steam, generated in the boiler, is led directly through the tube, D, into the other limb of the U-tube and passes thence through E into the calorimetric apparatus. If

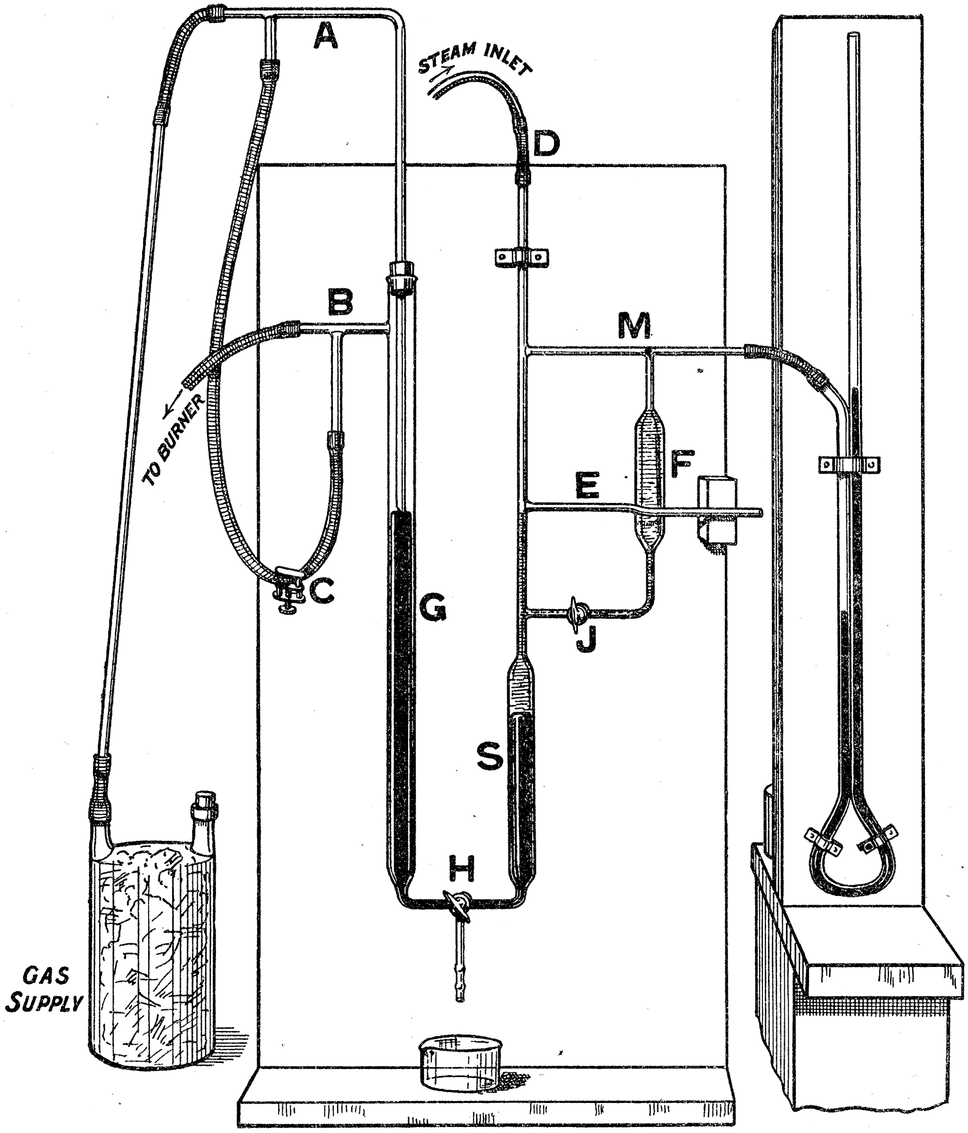

Fig. 6.

the connecting tap, H, be open, so that the columns of mercury in the two limbs, G and S, are connected, it is obvious that, as the steam pressure rises, the mercury will be forced downwards in S and upwards in G, until eventually the main supply of gas passing through the lower end of the tube, A, is more or less cut off. When the gas supply to the burner is thus reduced, the rate at which steam is generated is lessened, and in a few seconds equilibrium is attained; the current of steam keeping its own pressure constant. This pressure is measured on a manometer connected with the tube, M. Perfection in regulation is not obtained until sufficient water has condensed in the limb, S, to fill the length of tube between the top of the mercury and the exit, E, but to hasten this condition the tap, J, may be opened, thus allowing water which has condensed in the bulb, F (which is also connected to the tube, M) to run into the limb, S, until the latter is filled to the requisite height. The pressure of the steam can be altered either by varying the amount of mercury in the regulator, or by raising or lowering the end of the tube, A. At the end of every experiment the main gas supply was cut off and the tap, H, closed, so that when the regulator was put into action at the commencement of the next experiment, the limb, S, contained sufficient water to ensure perfect regulation at once. It is necessary for the gas supply to be constant, since variations in the pressure in the gas main produce corresponding variations in the quantity of steam generated. Such effects were not noticeable on the thermometric readings of the "cold temperature," but they were quite evident when the heating current was on. Sudden and violent fluctuations were prevented by passing the gas into the bell of a small gas-holder before it entered the regulator. The accuracy of these experiments depends chiefly on the constancy with which the pressure can be maintained, and the wonderful steadiness in the temperature of the steam is exemplified in the extended tables of observations which are given.

From these it will be seen that the "cold temperature," observed after an interval of about an hour, agrees to 0·03 cm. of bridge-wire or to about one two-hundredth of a degree Centigrade, with that determined before the electrical energy was supplied.

The Calorimetric Arrangements (fig. 7).

The calorimeter proper consisted of a glass tube, Y, about 50 cm. long, in which the heating coil, C, and the thermometer sheath, N, were fixed. This tube was jacketed by another glass tube, S, which enclosed the length occupied by the heating coil and thermometer. In the following experiments three different types of calorimeter were used, each of which will be described later in connection with the results obtained.

The calorimeter flow-tube and its surrounding glass sheath were carried on a split rubber cork wound with omega tape and fixed, making a steam-tight joint, into a space enclosed by a double-walled brass jacket, 45 cm. long and 5 cm. internal diameter. From the lower part of this jacket there was a double-walled side-tube 60 cm. long, packed tightly with gauze discs, through which the steam had to pass before it reached the calorimeter proper. The whole external jacket hence consists of two L-shaped vessels, one inside the other, the space between the double walls being continuous.

This space was provided with an inlet, E, connected directly on to the pressure regulator, and the steam entering here, passed between the double walls of the jacket and out at F into the steam separator, G, whence it entered, through the throttle, T, into the side-tube.

On its passage through the tightly packed gauze discs in the side-heating tube the steam was heated up to the temperature of the jacket. It then entered the space surrounding the calorimeter, whence it finally passes down the flow-tube, Y, to the condenser fixed on to Z. In fig. 7, which represents diagrammatically the arrangement thus described, it will be noticed that the cylindrical space inside the double walls of the main jacket is divided into two compartments by a brass disc, K. This was soldered round the inner tube about 5 cm. from the upper end. The function of this disc is to prevent the steam impinging on the rubber cork closing the upper end of the tube, and thus being cooled.

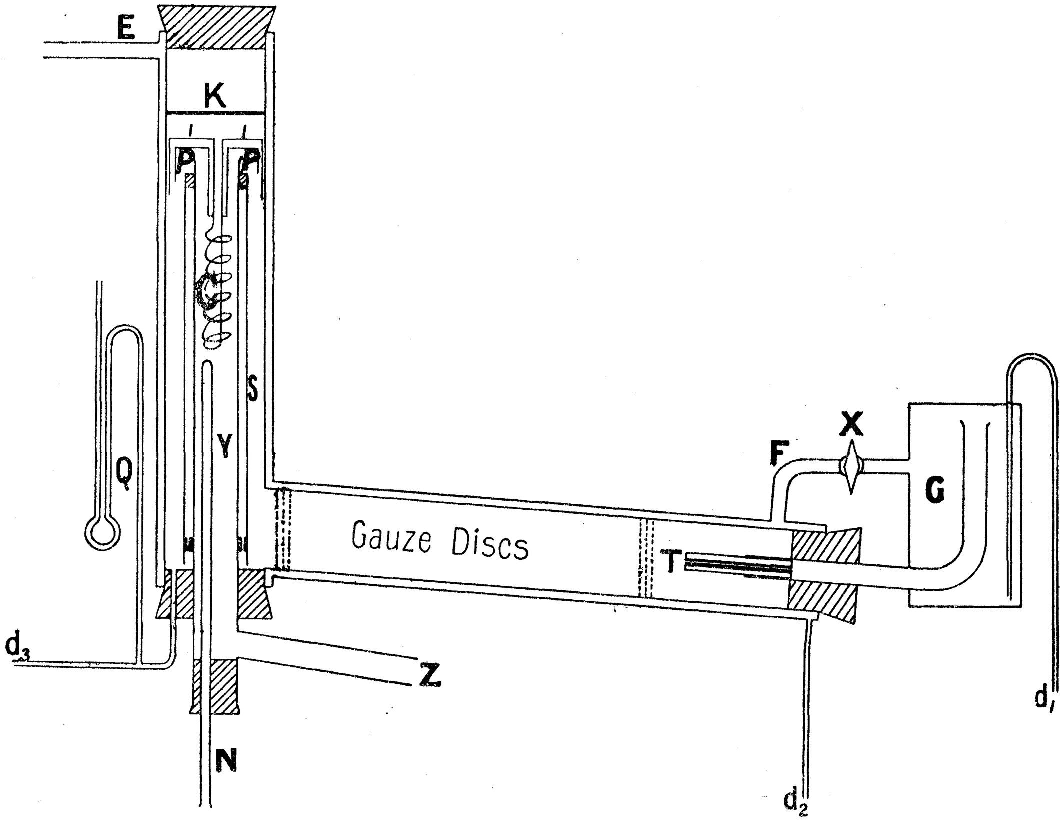

Fig. 7.

Any slight cooling due to the steam striking the lower split cork is of no importance, since the steam would be warmed again during its passage up between the calorimeter and the surrounding jacket. The whole of the jacket, the separator, and the connecting tubes were heavily lagged with felt. The main jacket containing the flow-tube was fixed vertically. The side-heating tube was thus slightly inclined to the horizontal, consequently, any water condensed between the double walls gravitates towards the drain-tube, d_2, whence it is expelled. The other drain-tubes, d_1 and d_3, serve to remove condensed steam from other parts of the apparatus.

The drains d_1 and d_2 consisted of lengths of about 2 metres of small-bore compo-tubing. The drain d_3 consisted of tubing of the same bore, but the lengths fixed here were altered according to the magnitude of the steam-flow in such a manner that there was always a small steady current of steam passing out from this drain. The drain-tube, d_3, was connected to a brass tube, 3 mm. diameter, carried by the split cork to which reference has been made, the end of the brass tube being flush with

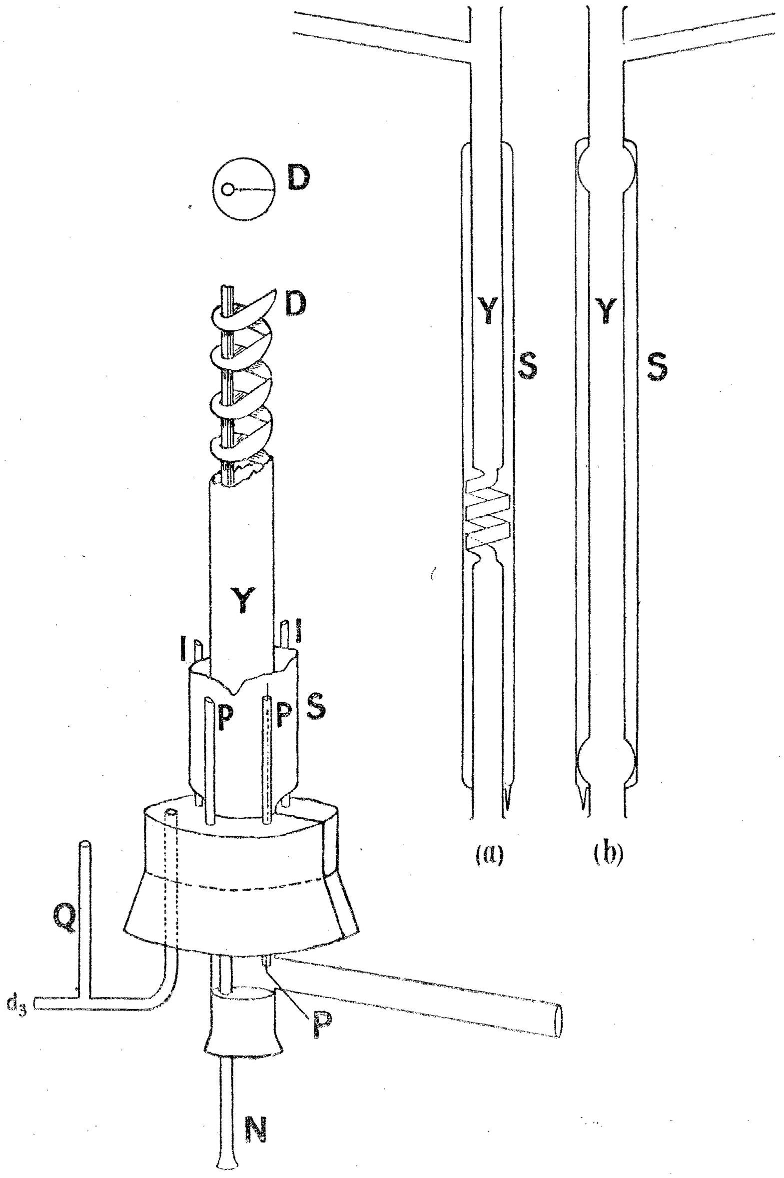

Fig. 8.

the inner surface of the cork. A water manometer, Q, was also attached to the brass tube so that an approximate estimate of the pressure in the space surrounding the calorimeter could be made.

The Heating Coil.

This consisted of about 130 cm. of 0·004-inch platinum wire, bent double, the two strands being wound, in parallel, on a serrated mica frame. The loop end was gold-soldered to a piece of 0·008-inch platinum wire which was fixed centrally along the mica framework. A length of 12 cm. of No. 22 silver wire, bent double, was joined at its loop to the free end of this thicker platinum wire, and the two other free ends of the 0·004-inch platinum wire were likewise soldered to the loop end of a similar piece of silver wire. These silver wires were bound to the mica frame, which was always immersed to a depth of 4 or 5 cm. in that part of the current of steam which was actually heated; thus any error due to conduction of heat from the heating coil was prevented. The four free ends of these silver wires were then soldered to the main current and potential leads. Each of these leads was a length of No. 20 copper wire, to the upper end of which was hard soldered about 1 cm. of No. 27 platinum wire. A thin lead glass tube enclosed each conductor and was fused round the platinum wire. The leads thus enclosed were brought down symmetrically around the glass jacket, S, surrounding the flow-tube, Y, and were carried by the split cork. The general arrangement is indicated in figs. 7 and 8, P P being the potential and I I the current leads.

The Thermometer.

This consisted of about 120 cm. of 0·004 inch platinum wire, wound in a screw thread of 40 turns per cm., cut on an ivory cylinder. This was carried on a long lead of No. 24 copper wire, the latter passing axially through to the far end of the cylinder. The cylinder was fixed in its position on the wire between two small lumps of solder. The ends of the platinum wire were soldered, one to the lower end of this lead, the other to the end of a length of No. 28 copper wire which only reached as far as the near end of the ivory cylinder. Another pair of leads, consisting of equal lengths of Nos. 24 and 28 copper wire, which again only reached as far as the near end of the cylinder, where their ends were soldered, formed the compensating leads of the thermometer. All these leads were enclosed in fine glass capillary tubes firmly bound together with silk. Before winding the platinum wire, the ivory was baked for some time at a temperature of about 120° C. in order to shrink the cylinder. The over-all length of the thermometer was 35 cm., the platinum wire being wound over a length of 3·6 cm. of ivory. The thermometer and leads were enclosed in a glass sheath, N (fig. 7), 2·5 mm. in diameter, which was carried by a rubber cork fixed tightly into the lower end of the flow-tube. This thermometer sheath reached right up the flow-tube to within a few millimetres of the lower end of the heating coil, so that by moving the thermometer up or down in its sheath, the distance between the end of the heating coil and the middle of the thermometer could be easily varied between wide limits. This thermometer was made by Mr. W. J. COLEBROOK, Superintendent of the Physics Workshop at the Imperial College, and here I desire to record my indebtedness to him for the assistance I have obtained during the construction of the apparatus used in this investigation.

The Platinum Thermometer Bridge and the Measurement of the Fundamental Interval and Stem-exposure of the Thermometer.

The well-known form of bridge designed by Prof. CALLENDAR was used, the plug contacts being replaced by mercury cups. Three calibrations of the coils and bridge-wire were made during the course of this investigation and corresponding readings in these different calibrations agreed to within 0·005 cm. of bridge-wire. An astatic galvanometer, with a long quartz fibre suspension, was used with the bridge, and the sensitiveness in the final experiments was such that by moving the contact maker 0·1 cm. on the bridge-wire, an alteration of from 10 to 15 divisions in the deflection was produced on reversing the current. Observations of the sensitiveness were made during each experiment, and no attempt was made to adjust the contact to obtain an exact balance. The usual apparatus was employed for the determination of the fixed points, and these were re-determined after every removal of the thermometer from its sheath. A series of observations of the freezing- and boiling-points, with various lengths of the thermometer stem exposed, was made. These values were plotted, and from the curves obtained the variation of the fundamental interval with stem-exposure could be deduced. The values obtained on September 12, 1912, were as follows :—

Exposure.	Freezing-point.	Boiling-point.	Fundamental interval.
cm.			
0	1381·65	1919·435	537·785
2	1381·655	1919·43	537·775
4	1381·665	1919·42	537·755
6	1381·675	1919·415	537·74
8	1381·70	1919·405	537·705
10	1381·73	1919·40	537·67
12	1381·80	1919·38	537·58
14	1381·95	1919·305	537·355
15·5	1382·18	1919·11	536·93

These results show that the fundamental interval only falls by about 1 part in 500 when the stem-exposure is changed from 0 to 16 cm. In the calculations, the values taken for the boiling-point and fundamental interval are those corresponding to the given amount of exposure. A few determinations of these constants obtained on different dates are included in order to show the constancy with which they could be repeated.

Date.	Freezing-point.	Boiling-point.	Fundamental interval.	Exposure.
1912.				cm.
April 18	1381·65	1919·46	537·81	3·5
September 12	1381·66 1381·71	1919·42 1919·40	537·76 537·69	3·5 8·7
November 14	1381·89	1919·58	537·69	8·7
1913.				
March 6	1381·85	1919·62	537·77	3·5

It will be noticed that there is an increase in the values of the freezing- and boiling-points but that the fundamental interval remains remarkably constant. The increased resistance is easily explainable. It is due to the slight squeezing of the wire against the side of the glass sheath, whereby a gradual reduction in the cross-section of the wire is produced after many movements of the thermometer in its sheath. During the autumn of 1913 the thermometer was broken; after mending, by fusing on a short length of the same kind of platinum wire, the constants were :—

Date.	Freezing-point.	Boiling-point.	Fundamental interval.	Exposure.
1914.				cm.
January 26	1383·45 1383·50	1921·74 1921·72	538·29 538·22	2 8
May 1	1383·55	1921·76	538·21	8

Methods used to Obtain a Uniform Temperature Distribution in the Steam Flow.

By far the most troublesome source of error to eradicate was that due to imperfect mixing of the steam. When it is remembered that the velocity with which the steam is flowing may be as great as 80 cm. per second, it is obvious, that in order to ensure a uniform radial distribution of temperature throughout the steam, in the short time of its passage from the heating-coil to the thermometer, the mixing arrangement must be extremely good. The only method of testing the excellence of the stirring arrangement is to conduct experiments with different distances between the heating-coil and the thermometer. Until agreement in the calculated values of the specific heat obtained under the different experimental conditions, and a definite relationship between the values of the heat-loss and the distances separating the heating-coil from the thermometer are obtained, it cannot be assumed that the mixing is adequate. The methods of mixing employed may be conveniently referred to as—(*a*) gauze mixing; (*b*) spiral mixing. The method (*a*) was employed by SWANN in his experiments on the Specific Heat of Air and Carbon Dioxide, and has been used by other observers in their determinations of specific heats by the continuous-flow method. Circular discs of copper gauze are cut with a diameter slightly greater than the internal diameter of the flow-tube. These discs are then bent just to fit the flow-tube, each disc having a small flange. The space between the heating-coil and the end of the thermometer tube is then filled with these discs, and since any one disc only touches the flanges of the discs on either side of it, longitudinal conduction from disc to disc is necessarily very small. At the same time, in virtue of the high thermal conductivity of copper, a uniform distribution of the heat throughout the gas, as it passes from the heater to the thermometer, might be expected. This method of mixing was employed in a large number of experiments extending over a period of more than two years. In some experiments, discs were also fitted over that part of the thermometer tube surrounding the ivory cylinder; in other experiments the thermometer previously described was replaced by a bare-wire thermometer consisting of a single loop of 0·001-inch platinum wire. Although, in most cases, very good agreement between the results of experiments under any given conditions was obtained, no such agreement was found between these results and those obtained under different conditions. A further consideration of the results obtained with this form of mixing will be found later.

(*b*) *Spiral mixing.*—A very efficient method of mixing the steam consisted in tightly wrapping around the thermometer tube a spiral of small bore compo-tubing, the walls of which were then pinched together to form a screw thread closely fitting the flow-tube and with a pitch of about 1 cm. The only apparent disadvantage of this was that conduction along the spiral might be considerable, so another form of spiral was designed in which this error was minimised.

The mixing arrangement as used in the final experiments is indicated in fig. 8. A number of circular discs, each one having a diameter equal to that of the flow-tube, were punched out of thin copper sheet. These were then clamped one above the other and a hole of diameter equal to that of the thermometer sheath was drilled eccentrically through all of them, fig. 8, D. Each disc was then cut along the diameter common to the disc and the hole, and was slipped on to the thermometer sheath. By slightly bending the discs in the manner shown, they, when soldered together, form a kind of spiral which mixes the steam most efficiently; moreover, since the discs are only connected by small solder junctions, longitudinal conduction is greatly reduced.

Determination of the Weight of Condensed Steam.

Prof. Callendar has shown the importance of obtaining steam free from impurities, hence only distilled water was used in the boiler. The steam passed to the calorimetric apparatus through block tin tubes, and the various joints were made in such a way that the steam came in contact with as little rubber as possible. After its passage through the calorimeter, the steam was led into a brass condenser more than 1 metre long. The water was collected in half-litre flasks, placed in such a manner that the end of the condenser was always 2 or 3 inches inside the flask. In all experiments the flasks were closed immediately after their removal from the condenser and then weighed. The question of the evaporation of the water during its condensation and collection was carefully considered. The air in the flasks was always fully saturated, since a certain amount of water remained in them from previous experiments, so that one would not expect any appreciable amount of evaporation during the actual collection of the water. Experiments were made in which, immediately after weighing a flask, it was uncorked, placed near the end of the condenser for a known time, and then weighed again. In no case was there a change in weight amounting to 0·03 gr. in 15 minutes. In some experiments the collecting flasks were fitted with corks, through which passed (*a*) a drying tube filled with calcium chloride; and (*b*) a tube which was only just wider than the nozzle of the condenser. Again no systematic differences were observed and, since the rapid adjustment of a flask under the end of the condenser was made less facile, in most of the experiments the flasks have been used without drying tubes. The weights were obtained by means of a large Oertling balance, sensitive to 0·01 gr. with 500 gr. on the scale-pan. It was sufficiently accurate to note the weights to 0·05 gr., care being taken that the total error on the difference between the weights (*i.e.*, flask alone and flask + water) was not cumulative. The maximum error on the weight determinations is not likely to be greater than 0·05 gr., or 1 part in 3000 on the minimum flow. The weights of water have been reduced to weights in vacuum; the air displaced being always fully saturated, its density under average conditions, viz., 760 mm., and at 15° C., has been taken as 0·00121 gr. per cubic centimetre.

Adjustment of the Flow.

The amounts of steam flowing through the calorimeter were adjusted by means of throttles, fig. 7, T. Each throttle consisted of a short length of glass tube which was tightly fixed, by means of a rubber tube and wire, into the outflow tube connecting the steam separator with the side-heating tube. The diameters of the throttles were such that the flows used were of the order of 0·8, 0·4, and 0·2 gr. per second.

Method of Making an Experiment.

The tap, H, fig. 4, between the two main limbs of the regulator was opened slightly, so that the level of the mercury in the tube in which the gas current is adjusted was lowered sufficiently to allow a full stream of gas to pass to the burner; this tap was then closed. As soon as the steam was generated it passed into the outer annular jacket surrounding the calorimeter, and a small current of steam escaped through the drain-tube, d_2. The pressure gradually rose until the difference between the levels on the gauge attached to M was the same as that between the levels of the mercury in the regulator, when the tap, H, was again opened and the regulator put into action. These conditions were maintained for about half-an-hour, in order that the copper discs in the side-heating tube and the calorimeter itself might be warmed up before passing steam into the inner jacket. At the end of this period the tap, X, fig. 4, was slowly opened, thus allowing steam to enter the separator and to pass through the throttle into the calorimetric apparatus. It was possible to obtain an approximate reading of the temperature of the boiling-point of steam under the given barometric conditions whilst this gradual heating up was taking place. For during this initial warming of the calorimeter by the inflowing current of steam a small amount of condensation necessarily took place in the flow-tube, this moisture being evaporated at a constant temperature after the passage of the steam for a few minutes.

At the end of about 40 minutes the thermometer reading was quite steady, and after making allowances for changes in the barometric height, agreed to within 0·03 cm. of bridge-wire with the cold temperature reading taken after the heating. In some of the earlier, and in all the final, experiments, these "initial cold temperatures" were recorded until the indicated temperature was steady for about ten minutes, but since it was found that the cold temperatures obtained after the heating (*i.e.*, three-quarters to one hour later) agreed so well with the initial values, in many experiments these initial readings were not recorded but only noted, so that it was known when the calorimeter was heated up, and the conditions practically constant. The electric current was then started through the heating coil, adjusted to give the desired rise of temperature, and approximate balances noted on the potentiometer. After another interval of from 20 to 40 minutes, depending on the flow, the balance-point on the bridge again became steady to about 0·02 cm. or 0·004° C., and the main calorimetric observations were commenced. At a definite instant a weighed half-litre flask was put under the end of the condenser, left there for exactly ten minutes, in the case of the maximum flow, and then taken away. Ten seconds afterwards it was replaced by another flask, and a second observation of the flow during another ten-minute interval was taken. The duration of the experiments with the medium and minimum flows was 15 minutes. In most cases the amounts of steam condensed in two consecutive experiments, under as nearly as possible identical conditions, agree to about 1 in 1000, but when the difference in the observed flows was greater than this, due to some real change in the current of steam, the variation had often been expected, since a change in the temperature readings, not due to a change of barometric pressure nor to a change in the rate of supply of electrical energy, had pointed to such an effect. The readings of the thermometer were taken at every even minute, the contact on the bridge-wire being set at the nearest millimetre, and the deflection of the galvanometer noted on reversal of the current.

During every experiment several readings were taken with the contact made at the next millimetre reading on the bridge which gave a galvanometer deflection in the opposite direction. The height and temperature of the barometer were read at intervals of about seven minutes, unless they were varying very rapidly, when readings were taken more frequently. The approximate value of the current was noted on the ammeter; a knowledge of this was useful when adjusting the current in the determination of the heating effect of the leads. The potential balances across the standard cells, across the secondary standard resistance, and across the heating coil were taken at intervals during the experiment. In addition, the temperature of the standard cells and that of the oil bath in which the secondary standard was placed, were noted. Since seven Leclanché cells were required in the maximum flow, and only five in the medium and minimum flows, a small steady change took place in the potentiometer reading for the standard cells during the short interval following the change in the number of Leclanchés used. The variation was only 3 or 4 parts in 7000 in about half-an-hour, and after that period of time had elapsed the reading remained quite constant. The potential balances across the heating coil and across the secondary resistance were wonderfully steady, especially during experiments with the two smaller flows. In the case of the maximum flow the irregular fluctuations only amounted to about 30 divisions on each side of the balance-point on the galvanometer scale, and a change in the potentiometer reading of 4 (in about 8000) was sufficient to throw the balance out by the same amount. At the end of the second experiment with any flow, the electric current was switched off and the weights of condensed steam determined. As soon as the temperature was again nearly steady, another flask was put under the end of the condenser and a "check" flow obtained. Meanwhile temperature readings were taken until the recorded values were constant. This temperature reading is tabulated as "cold temperature before." A current equal to that used in the main experiments was then passed through each pair of current and potential leads, and the heating effect of the current in each pair of leads measured. Then the cold temperature was again determined: this value is tabulated as "cold temperature after." I have included specimen tables showing all the observations made on one day, for thereby the remarkable steadiness of the conditions is illustrated very clearly.

Reduction of the Observations.

In each experiment there are as many observations of the "hot temperature" as there are minutes of time in the duration of the flow, and, in addition, there are the two "cold temperatures," the barometric readings, the various temperature observations and the potential balances. The mean value of each set of readings is then obtained, thus correcting them to the middle of the interval in order to correspond to the time of average flow. The potential readings were not taken as frequently as the thermometric readings, this being unnecessary, since the latter were irregular whilst the former gradually changed in one definite direction; they generally showed a slight fall. The electrical energy supplied per second was determined from the mean values of the potentiometer readings; the necessary temperature corrections for the resistance of the standardised coil and the E.M.F. of the cadmium cells having been previously made. The mean thermometric readings give the temperatures of the steam when hot and when cold, and from other measurements the rise of temperature due to the heating effect of the current in the leads connected to the heating coil can be obtained. All these temperatures are expressed in terms of centimetres of the bridge-wire, the calibration corrections of the bridge itself being included.

The rise of temperature due to the passage of the current through the leads is subtracted from the observed "hot temperature," the value thus obtained and the mean "cold temperature" are then reduced to platinum temperatures, and these again to temperatures measured on the air scale, the latter reduction being made by means of the well-known parabolic formula $t-pt = 1{\cdot}50\times 10^{-4}t\,(t-100)$. The flows given are corrected to correspond to weighings *in vacuo*.

The number of flows taken for a complete experiment was always *three*, each flow being repeated twice. The concordance between the values of $\mathrm{CE}/\mathrm{Q}d\theta$, calculated from two consecutive flows of the same magnitude, gives a criterion of the accuracy of the experimental measurements. Whenever possible, three flows were taken on the same day, as it was thought that the heat-loss might vary from day to day; also the order of the flows was usually medium, minimum, maximum, in order to reduce the time taken between experiments made with different flows. For when the flows are taken in this order, the initial heating up is fairly quick, and less time is lost in refilling and reheating the boiler between successive flows. Hence there is no long interval during which steam is not passing round the outer jacket, and the calorimeter does not cool to any very great extent between consecutive experiments. Even when taking the flows in this order it was impossible to complete the three experiments in less than eight hours.

Preliminary Experiments.

A long series of preliminary experiments was made in order to find the best method of mixing the steam, to investigate the relationships between the heat-loss and the flow, and between the heat-loss and the distance separating the thermometer from the heating coil. Several different arrangements of the apparatus were made, and various methods of stirring employed. It will suffice to summarise these experiments in the order in which they were carried out, by referring to the main details and arrangement of the calorimetric apparatus, and to the results obtained. All the results quoted have been calculated in the same way as in the final experiments.

(*a*) A few experiments were made with the apparatus used by SWANN for air and described by him in his paper. In this arrangement bare wire thermometers, wound on mica frames, were used. No satisfactory results were obtained owing to the condensation of steam upon the mica frames and the consequent impairment of their insulating properties.

(*b*) The apparatus was dismantled and set up again with a single thermometer (that used in the final experiments) enclosed in a glass sheath passing *centrally* along the flow-tube and carried by a rubber cork fixed in the outflow end of the tube. The stirring arrangement consisted of the pinched spiral of compo-tubing, to which reference has been made. The main flow-tube was fixed vertically, as is indicated in fig. 7, with the non-vacuum jacketed sheath.

The current and potential leads entered the flow-tube in the manner indicated in this figure, but they were carried by a cork (see SWANN's paper, fig. 1) fitting into the top of the outer brass jacket, and were not bent round and carried down outside the flow-tube as in fig. 7. The disc, K, had not been soldered across the jacket at this time, but its function was performed by a rubber bung which fitted tightly to and was carried by the current and potential leads. The initial temperature of the steam was about 103° C., and the three flows varied from 0·57 to 0·14 gr. per second. The values of the constants deduced were

$$S_c \text{ at } 103^\circ \text{C.} = 2{\cdot}021, \qquad h = 0{\cdot}0400, \qquad k = 0{\cdot}00400.$$

In these experiments the heating coil had a resistance of about an ohm, and the standard resistance used as a comparison was 1·039 ohms at 19° C. The temperature variation of the specific heat was about 0·0035 per degree, a value three times as great as that found in the later experiments. Later, the separator was re-designed, and in all the subsequent experiments it was of the form shown diagrammatically in fig. 7. A new heating coil and a new standardised coil of about 5 ohms resistance were made and used in all the experiments made afterwards. In addition, the regulator was altered to give a "cold temperature" of 104·5° C. instead of 103° C. The effect of these changes was to reduce the temperature coefficient of the specific heat to about 0·0010 joules per degree.

(*c*) Many experiments were made in which the temperature of the steam was measured by means of a bare wire thermometer consisting of about 3 cm. of 0·001-inch platinum wire. Spiral mixing was impossible, and in consequence the gauze method of mixing was employed. Measurements of the heating effect of the current in the thermometer were made. It was found that although this heating effect was slightly different in the different flows, it was the same on both hot and cold temperatures observed with any one flow, and no systematic error was thereby introduced. The apparent values of the specific heat obtained with various amounts of gauze and with the above arrangement of apparatus ranged about 1·95, gradually increasing as more gauze discs were inserted.

(*d*) Further experiments with gauze mixing were carried out with the calorimeter and jacket, arranged as in fig. 7, and with the enclosed thermometer used in the earlier and in all the later experiments.

That part of the thermometer sheath surrounding the ivory bulb of the platinum thermometer carried gauze discs, a variable number of similar discs being interposed between the end of the heating coil and the end of the thermometer tube. With 4·5 cm. length of discs on the thermometer tube, and a length of 7 cm. of the total distance between the *end* of the thermometer and the heating coil filled with similar discs, the value of S_c calculated from the experimental observations increased (approximately proportionately) with the actual distance between the heating coil and the thermometer. Again, with a distance of about 14 cm. between heating coil and thermometer, the calculated value of the specific heat increased with the length of tube filled with gauze, the latter variation being from 1·965 with 4·7 cm. of gauze to 1·990 with 10 cm. of gauze. These results show that, in order to mix the steam thoroughly by means of gauze discs, a much greater distance must exist between the thermometer and heating coil than was possible in this arrangement without having a great length of the thermometer-stem exposed. Further experiments on gauze mixing were not made for the above reason, and also because, in order to change either the position of the thermometer or the amount of gauze, it was necessary to dismantle the calorimeter.

The Final Experiments.

These may conveniently be divided into two groups: one consisting of the experiments made with the non-vacuum jacketed calorimeter, the other group including all the experiments performed with the different types of vacuum vessel. Abridged tables of the experimental measurements are to be found below (p. 425). Complete records of all the observations are preserved in the Archives.

Group 1. *Experiments with the Non-vacuum Jacketed Calorimeter.*—Fig. 7 shows the general arrangement of the calorimetric apparatus during the course of these experiments. The thermometer was fixed *eccentrically* in the spiral constructed of discs of copper foil. The conditions under which the experiments in this group were made were varied considerably. The group itself consists of four series of experiments which only differ in that the heat-loss has been progressively augmented by increasing the distance between the heating coil and the thermometer by sliding the latter in its enclosing sheath. In each series three flows were used, and at least two different values of the rise of temperature.

Group 2. *Experiments with Vacuum-jacketed Calorimeters.*—The general arrangement was as in the last group of experiments and as indicated in figs. 7 and 8.

There are two series of experiments in this group: one series (a) in which the vacuum-jackets were exhausted before their insertion in the double-walled brass jacket, and a later series (b) with the silica calorimeter, in which case the vacuum was formed when the calorimeter was *in situ*. In this case the space between the double walls of the calorimeter was connected with a Geissler tube, a charcoal tube, and a pump. Three sets of experiments were made with different pressures in this jacket.

Calculation of the Results.

The values of $\mathrm{CE/Q}\,d\theta$, obtained with three different flows, but with the same rise of temperature $d\theta$, were calculated from the reduced tables of observations, and then, by means of three equations of the form

$$\mathrm{CE}/d\theta = \mathrm{S}_m\mathrm{Q} + h + k/\mathrm{Q},$$

the values of S_m, h, and k were obtained. S_m is the mean specific heat over the range 104·5° C. to $(104{\cdot}5 + d\theta)°$ C. Similar calculations were then made from the results obtained under the same experimental conditions but with other values of $d\theta$, and it was found that, although the values of h and k were constant within the limits of experimental error, the values obtained for S_m decreased with an increase in the value of $d\theta$. This relation is represented by the equation

$$\mathrm{S}_c = \mathrm{S}_m + 0{\cdot}0010\,d\theta.$$

S_c = specific heat at the cold temperature, *i.e.*, 104·5° C.

This means that, for any given flow with a given calorimetric arrangement, each quantity $\mathrm{CE/Q}\,d\theta$ depends on the magnitude of $d\theta$, hence by applying this temperature correction to the observed values of $\mathrm{CE/Q}\,d\theta$ the latter are brought to the values they would have had if the rise of temperature had been zero. Then, by taking the mean of all the maximum, all the medium, and all the minimum values of $\mathrm{CE/Q}\,d\theta$, thus corrected, and substituting these in the three above equations, the most probable values of S_c, h, and k can be deduced. The values of S_c thus obtained show a distinct variation with the barometric height. This variation of the specific heat at constant pressure with pressure can be calculated by means of equation (7), p. 387. In the case of steam, at a temperature of 104·5° C., if S is expressed in joules/gr. deg., and 1 cm. of mercury is taken as the unit of pressure $d\mathrm{S}/dp = 0{\cdot}0013$, this means an increase in the value of S of 0·065 per cent. for an increase of pressure of 1 cm. of mercury. Experimentally, the value of $d\mathrm{S}/dp$ is found to be about twice as great as this, but, taking into consideration both the smallness of the correction and the fact that the barometer only varied by about 2 cm. during any one series of experiments under identical conditions, the agreement is very satisfactory. A pressure correction of 0·1 per cent. per centimetre has been applied to the results calculated as above in order to reduce them to the values corresponding to a pressure of one atmosphere. The variation of the specific heat with temperature, indicated by the experiments made with different values of $d\theta$, was directly measured in the case of each calorimetric arrangement in the following manner. With a constant value of the flow a series of experiments was made in which only the value of $d\theta$ was changed. The observations made in the case of two such experiments with the medium flow are given (fig. 9).

In the results quoted, the observed values of $\mathrm{CE/Q}\,d\theta$ have been corrected to correspond to an infinite value of the flow and the pressure correction has been applied. These corrected values of $\mathrm{CE/Q}\,d\theta$ are the values of the mean specific heat S_m. The relationship existing between the values of S_m and $d\theta$ is well represented by the equation previously given. Similar experiments have been made with both the maximum and minimum flows and the observed temperature variation found in each case agrees with that given above. In some experiments a more rapid variation of the mean specific heat with temperature, in the neighbourhood of the cold temperature, has been indicated, but with small values of $d\theta$, the experimental errors are magnified, and in consequence, the straight line relationship has been applied to all the observations. The temperature variation of the specific heat at the constant pressure of one atmosphere as calculated from equation (7) gives $d\mathrm{S}/d\theta = -0{\cdot}0010$ or $\mathrm{S}_\theta = \mathrm{S}_c - 0{\cdot}0010\,d\theta$ where S_θ is the actual specific heat at the temperature θ. Hence the observed coefficient is double that deduced from theoretical considerations. The experimental

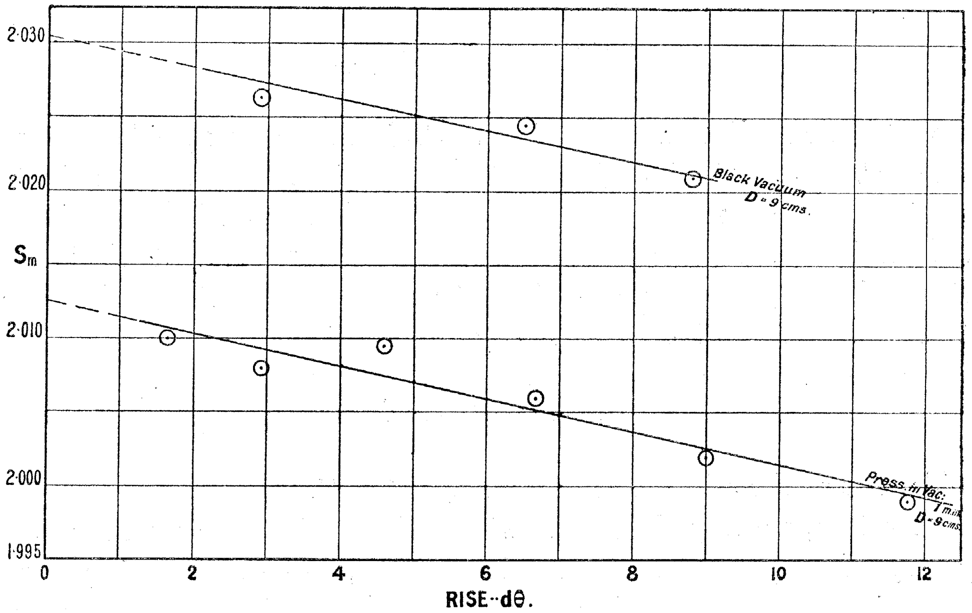

Fig. 9.

value has been used in reducing the mean specific heats to the value corresponding to zero rise of temperature.

Throttling Effects in the Calorimeter Flow-Tube.

During its passage between the heating coil and the thermometer the steam expands adiathermally and its temperature is lowered. This effect depends on the actual temperature of the steam and, in consequence, the cooling will be different on the hot and the cold flows; it is greater on the cold flow. However, it is only the *change* in the amount of cooling which affects the results systematically; the correction is such that it raises the observed value of the specific heat. The pressure drop between the heater and the thermometer was estimated from the indications of the manometer, Q, and the variation of the cooling effect was calculated from equation (6), p. 387. With the straight flow-tube calorimeters the difference in the cooling effects is about 0·0035° C. for a rise of temperature of 10° C. in the case of the maximum flow, and for the medium and minimum flows the differences are still smaller. Hence the throttling effects in the straight flow-tube calorimeters are quite negligible. An additional proof that this is the case is afforded by the results of the experiments made with these calorimeters, with different distances, D, separating the thermometer from the heating coil. The mean values of the specific heat show no systematic variation with D greater than 0·1 per cent. and this is of the order of accuracy of the experimental measurements. With the spiral flow-tube calorimeter the cooling effects were larger, for they depend on the throttling occurring in the spiral, and the pressure differences between the heating coil and the thermometer were greater than in the case of the experiments made with the straight flow-tubes. An approximate calculation showed that the systematic error introduced, due to the neglect of these throttling effects, could not amount to more than 0·1 per cent. on the specific heat. Only one set of observations was made with the spiral flow-tube calorimeter and these experiments are, in comparison with the others, unimportant, and as the throttling correction is small and rather uncertain it has not been made.

(I designed the spiral flow-tube to be of such dimensions that the throttling effects would be negligible, but in the piece of apparatus supplied by the makers the spiral tube was constricted along its entire length.)

Specimen Tables of Observations.

A complete set of the observations made on May 1st, 1914, with the silica calorimeter, is included in order to show the steadiness of the experimental conditions. The vacuum jacket was exhausted by means of charcoal in liquid air, and throughout the three experiments no discharge could be produced in the Geissler tube connected with the jacket. The order in which the observations were taken has been described on p. 414. The values of S_c, h, and k calculated from these observations, after the necessary corrections have been made, are 2·0309, 0·00470 and −0·00005 respectively.

BLACK VACUUM. May 1st, 1914. Maximum Flow.

Temperature Observations.

Initial cold temperature. Box coils 1940·94.

Time.	Barometer.	B.W.	Deflection.
h. m.	° C.		
3 15		4·70	8 –
17			5 –
19	770·15		6 –
	19		
20			7 –
22			7 –
23		4·60	7 +
25			7 +

Hot temperature (C = 1·48 amps.). Box coils 1990·98.

Time.	Barometer.	B.W.	Deflection.
h. m.	° C.		
3 35	770·3	0·30	1 +
36	19		2 +
37			0
38			1 +
39			4 +
40			3 –
41			9 –
42			9 –
43			8 –
44	770·35		7 –
45	19		4 –
46			7 –
47			7 –
48			5 –
49			5 –
50			7 –
51			6 –
52			6 –
53			4 –
54	770·35		4 –
55	19		5 –
56			5 –
57			2 –
58			2 +
59	770·4		2 +
4 00	19		1 +
1			0
2			3 –
3			4 –
4		0·20	11 +
5	770·35		11 +
	19		

Cold temperature (before). Box coils 1940·94.

Time.	Barometer.	B.W.	Deflection.
h. m.	° C.		
4 9		4·70	23 +
10			12 +
11			6 +
12			3 +
13			0
16	770·4		1 –
18	19		3 –
20			2 –
22			2 –

Leads (C = 1·48 amps.).

Time.	Barometer.	B.W.	Deflection.
25		4·80	4 +
27			5 + (1)
29	770·35		5 +
	19		
31			6 +
33			6 + (2)
35			5 +

Cold temperature (after).

Time.	Barometer.	B.W.	Deflection.
39		4·70	0
42	770·4		0
45	19		0

Weight Determinations.

gr.	h. m. s.	gr.	h. m. s.	gr.	h. m. s.	gr.	h. m. s.
527·65	3 45 0	530·30	3 55 10	540·45	4 5 20	528·00	4 22 0
54·00	3 35 0	56·70	3 45 10	66·90	3 55 20	54·10	4 12 0
473·65		473·60		473·55		473·90	
Q = 0·7894 gr./sec.		Q = 0·7893 gr./sec.		Q = 0·7893 gr./sec.		Q = 0·7898 gr./sec.	

Potentiometer Readings.

5 Cadmium cells.	Temperature.	Time.	Standard resistance.	Temperature.	Time.	Heater.	Time.
	° C.	h. m.		° C.	h. m.		h. m.
4937	16·3	3 34	7261	31·0	3 35	8965	3 36
4937		40	7261		41	8964	41
			7260		47	8964	46
4937		54	7259		53	8963	54
4937	16·3	4 3	7258	30·8	4 5	8962	4 4

BLACK VACUUM. May 1st, 1914. Medium Flow.

Temperature Observations.

Initial cold temperature. Box coils 1940·94.

Time.	Barometer.	B.W.	Deflection.
h. m.	° C.		
9 40		5·80	6 +
42			12 +
48		6·10	0
50			6 +
52			11 +
53		6·20	0
57	768·75		5 +
58	17·5		3 +
10 2			5 +
3		6·30	8 −
5			9 −

Hot temperature (C = 1·04 amps.). Box coils 1990·98.

Time.	Barometer.	B.W.	Deflection.
h. m.	° C.		
10 30		1·80	4 −
31	768·9		4 −
32	17·5		1 −
33			2 +
34			5 +
35			3 +
36			1 +
37			1 +
38			1 +
39		1·90	13 −
40	768·9		12 −
41	17·5	1·80	2 +
42			3 +
43			3 −
44			4 −
45			4 −
46			4 −
47			3 −
48			2 −
49			2 −
50	768·9		2 −
51	17·5		1 −
52			1 −
53			1 −
54			0
55			0
56			1 −
57			1 −
58			2 +
59	769·0		1 −
11 00	17·5	1·70	12 +

Cold temperature (before). Box coils 1940·94.

Time.	Barometer.	B.W.	Deflection.
h. m.	° C.		
11 7		6·30	9 +
8			5 +
9			2 +
10	769·0		0
12	18		2 −
14			3 −
16			4 −
19			3 −

Leads (C = 1·04 amps.).

Time.	Barometer.	B.W.	Deflection.
23		6·40	3 +
25	769·2		6 +
26	18		12 + (1)
27		6·50	1 −
29			2 −
30	769·25	6·50	3 −
31	18		4 − (2)
33			3 −

Cold temperature (after).

Time.	Barometer.	B.W.	Deflection.
36		6·30	8 +
37			4 + (1)
39	769·35		5 +
41	18·5		5 +
44			6 +
46	769·4		7 + (2)
48	18·5		7 +

Weight Determinations.

gr.	h.	m.	s.
393·85	10	45	0
54·15	10	30	0
339·70			

Q = 0·3774 gr./sec.

gr.	h.	m.	s.
397·15	11	0	10
57·35	10	45	10
339·80			

Q = 0·3776 gr./sec.

gr.	h.	m.	s.
408·85	11	23	0
69·20	11	8	0
339·65			

Q = 0·3774 gr./sec.

Potentiometer Readings.

5 Cadmium cells.	Temperature.	Time.	Standard resistance.	Temperature.	Time.	Heater.	Time.
	° C.	h. m.		° C.	h. m.		h. m.
6946	16·6	10 29	7119	25	10 30	8668	10 30
6946		36	7118		37	8668	37
			7117		44	8667	44
6946		48	7116		49	8666	50
6946	16·5	59	7115	25	58	8665	57

BLACK VACUUM. May 1st, 1914. Minimum Flow.

Temperature Observations.

Initial cold temperature. Box coils 1940·94.

Time.	Barometer.	B.W.	Deflection.
h. m.	° C		
12 22		7·10	7 +
25	769·7		12 +
26	18·5	7·20	2 +
28			4 +
33	769·75		4 +
35			3 +
37			3 +
38	769·75	7·30	11 −
40	18·5		11 −

Hot temperature (C = 0·74 amps.). Box coils 1990·98.

Time.	Barometer.	B.W.	Deflection.
h. m.	° C		
1 5		4·30	4 +
6			6 +
7	769·75		3 +
8	18·5		7 +
9			3 +
10			3 +
11			4 +
12	769·8		1 +
13	18·5		2 +
14			2 +
15			2 +
16		4·40	11 −
17		4·30	2 +
18			3 +
19			4 +
20	769·8		5 +
21	18·5		5 +
22			5 +
23			4 +
24			4 +
25			3 +
26			3 +
27			3 +
28			5 +
29			4 +
30	769·9		4 +
31	18·5		4 +
32			6 +
33			7 +
34			8 +
35	770·0		7 +
36	18·5	4·40	7 −

Cold temperature (before). Box coils 1940·94.

Time.	Barometer.	B.W.	Deflection.
h. m.	° C		
1 44		7·30	21 +
45			9 +
46			4 +
47	770·0		1 +
49	19		4 −
52			7 −
54			9 −
56	769·9		9 −
59	19		10 −

Leads (C = 0·74 amps.).

Time.	Barometer.	B.W.	Deflection.
2 4		7·40	0
6			2 + (1)
8			2 +
9			4 +
10	770·0		5 + (2)
13	19		4 +

Cold temperature (after).

Time.	Barometer.	B.W.	Deflection.
16		7·30	2 −
18	770·0		6 −
20	19		7 −
24			7 −
27			6 −

Weight Determinations.

gr.	h.	m.	s.
214·90	1	20	0
54·40	1	5	0
160·50			

Q = 0·1783 gr./sec.

gr.	h.	m.	s.
217·95	1	35	10
57·50	1	20	10
160·45			

Q = 0·1783 gr./sec.

gr.	h.	m.	s.
228·95	2	0	0
68·70	1	45	0
160·25			

Q = 0·1781 gr./sec.

Potentiometer Readings.

5 Cadmium cells.	Temperature.	Time.	Standard resistance.	Temperature.	Time.	Heater.	Time.
	° C	h. m.		° C.	h. m.		h. m.
6945	16·5	1 4	5010	21	1 5	6075	1 6
6945		11	5009·5		11	6074·5	12
6945		16	5009		18	6074	18
6945		27	5009		26	6074	26
6945	16·5	33	5008·5	21	33	6073·5	34

Abridged Tables for the Calorimetric Experiments.

The following tables contain a summary of the observations. The original tables, from which these have been abridged, are preserved in the archives with the reduced tables referred to on p. 416. The second column gives the rise of temperature $d\theta$, corrected to the absolute scale. The third column gives the flow in grammes per second. In column four is each value of $CE/Q\,d\theta$ as obtained from the experimental observations, this quantity being expressed in joules per gr. deg. C. The next column gives $CE/Q\,d\theta$ reduced to the standard temperature 104·5° C., and to a barometric pressure of 760 mm. Column 6 gives the heat-loss expressed in joules per gr. deg. C., *i.e.*, H/Q, the quantity H being the sum of the terms h and k/Q. In the last column are the experimentally determined values of the specific heat of steam under atmospheric pressure at a temperature 104·5° C. After the completion of the experiments with the non-vacuum jacketed calorimeter it was thought advisable to design a vacuum calorimeter in order to determine whether the magnitude of the k term could be reduced. In consequence I designed the spiral calorimeter which was used as soon as it arrived. After these experiments I designed the straight vacuum jacketed flow-tubes which were exhausted by the makers. In experiments made with these calorimeters the value of k was not so small as in the previous experiments with the spiral calorimeter, and six more glass calorimeters were obtained which I hoped to evacuate *in situ*. Unfortunately, each one cracked during the initial heating and no experimental results were obtained until the silica calorimeter was set up.

Non-vacuum Jacketed Calorimeter. D = 11·5 cm.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
1912 April 23	5·057	0·8187	2·0689	2·0718	0·0566	2·0152
	5·057	0·8196	2·0651	2·0680		2·0114
April 25	5·316	0·7891	2·0683	2·0727	0·0591	2·0136
	5·308	0·7894	2·0687	2·0731		2·0140
April 29	8·521	0·7938	2·0647	2·0721	0·0587	2·0134
	8·499	0·7940	2·0653	2·0727		2·0140
April 25	5·332	0·3829	2·1492	2·1534	0·1400	2·0134
	5·330	0·3826	2·1488	2·1530		2·0130
April 29	9·133	0·3802	2·1477	2·1565	0·1411	2·0154
	9·109	0·3804	2·1479	2·1567		2·0156
April 25	5·538	0·1798	2·3899	2·3948	0·3839	2·0109
	5·534	0·1794	2·3948	2·3997		2·0158
April 29	9·058	0·1793	2·3930	2·4016	0·3847	2·0169
	9·035	0·1794	2·3940	2·4026		2·0179

Mean $S_c = 2·0143$, $h = 0·0400$, $k = 0·00520$.

D = 8·7 cm.

April 30	5·210	0·7956	2·0422	2·0457	0·0298	2·0159
	5·208	0·7964	2·0413	2·0448		2·0150
	5·210	0·7961	2·0414	2·0449		2·0151
May 2	8·970	0·7913	2·0338	2·0425	0·0301	2·0124
	8·966	0·7911	2·0346	2·0433		2·0132
April 30	5·157	0·3841	2·0905	2·0941	0·0801	2·0140
	5·153	0·3837	2·0923	2·0959		2·0158
May 2	8·935	0·3784	2·0859	2·0949	0·0818	2·0131
	8·931	0·3783	2·0870	2·0960		2·0142
April 30	5·078	0·1819	2·2618	2·2656	0·2497	2·0159
	5·074	0·1818	2·2628	2·2666		2·0169
May 2	8·984	0·1836	2·2538	2·2630	0·2482	2·0148
	8·982	0·1835	2·2544	2·2636		2·0154

Mean $S_c = 2·0147$, $h = 0·0172$, $k = 0·00520$.

Non-vacuum Jacketed Calorimeter. D = 6·2 cm.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
1912 May 8	9·230	0·7928	2·0193	2·0266	0·0125	2·0141
	9·223	0·7931	2·0179	2·0252		2·0127
May 9	5·147	0·7972	2·0236	2·0275	0·0123	2·0152
	5·143	0·7976	2·0230	2·0269		2·0146
	5·141	0·7980	2·0221	2·0260		2·0137
May 16	7·703	0·7891	2·0194	2·0285	0·0126	2·0159
	7·703	0·7891	2·0199	2·0290		2·0164
May 6	9·000	0·3801	2·0506	2·0595	0·0447	2·0148
	9·000	0·3800	2·0497	2·0586		2·0139
May 9	4·975	0·3847	2·0554	2·0590	0·0437	2·0153
	4·969	0·3850	2·0546	2·0582		2·0145
May 16	6·157	0·1823	2·1842	2·1916	0·1744	2·0172
	6·157	0·1824	2·1825	2·1899		2·0155
May 16	10·311	0·1826	2·1744	2·1861	0·1742	2·0119
	10·307	0·1826	2·1748	2·1865		2·0123
	Mean S_c = 2·0145,		h = 0·0033,		k = 0·00520.	
			D = 13·8 cm.			
May 23	9·460	0·7841	2·0829	2·0937	0·0811	2·0126
	9·458	0·7840	2·0827	2·0935		2·0124
May 30	9.463	0·7861	2·0845	2·0949	0·0808	2·0141
	9·457	0·7861	2·0850	2·0954		2·0146
June 6	5·606	0·8031	2·0846	2·0911	0·0789	2·0122
	5·595	0·8026	2·0873	2·0938		2·0149
May 24	8·693	0·3901	2·1870	2·1945	0·1800	2·0145
	8·684	0·3902	2·1862	2·1937		2·0137
May 30	9·156	0·3881	2·1828	2·1932	0·1811	2·0121
	9·150	0·3882	2·1820	2·1924		2·0113
June 6	5·217	0·3883	2·1900	2·1967	0·1810	2·0157
	5·208	0·3886	2·1885	2·1952		2·0142
May 23	9·254	0·1838	2·4633	2·4739	0·4635	2·0104
	9·250	0·1838	2·4631	2·4737		2·0102
	5·940	0·1840	2·4649	2·4722	0·4627	2·0095
May 30	9·268	0·1846	2·4650	2·4756	0·4607	2·0149
	9·264	0·1847	2·4630	2·4736		2·0129
June 6	5·261	0·1866	2·4653	2·4721	0·4544	2·0177
	5·257	0·1865	2·4665	2·4733		2·0189
	Mean S_c = 2·0135,		h = 0·0569,		k = 0·00520.	

Spiral Vacuum Calorimeter.

Length of path between end of heater and middle of thermometer, approximately 30 cm.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
1912. November 28	7·803 7·799	0·6457 0·6457	2·0779 2·0789	2·0861 2·0871	0·0599	2·0262 2·0272
November 30	7·768 7·766	0·6372 0·6366	2·0774 2·0779	2·0867 2·0872	0·0607	2·0260 2·0265
December 2	10·341 10·341	0·6427 0·6423	2·0791 2·0792	2·0892 2·0893	0·0601	2·0291 2·0292
December 9	7·203 7·211	0·6249 0·6237	2·0836 2·0837	2·0897 2·0898	0·0619	2·0278 2·0279
November 21	7·944 7·940	0·3502 0·3501	2·1313 2·1324	2·1380 2·1391	0·1140	2·0240 2·0251
November 25	10·170 10·170	0·3472 0·3467	2·1297 2·1314	2·1405 2·1422	0·1151 0·1156	2·0254 2·0266
December 9	7·106 7·112	0·3535 0·3529	2·1347 2·1351	2·1415 2·1419	0·1130	2·0285 2·0289
November 21	7·805 7·805	0·1665 0·1665	2·2791 2·2798	2·2858 2·2865	0·2601	2·0257 2·0264
November 25	10·119 10·117	0·1655 0·1655	2·2752 2·2745	2·2863 2·2856	0·2619	2·0244 2·0237
December 9	7·020 7·018	0·1677 0·1673	2·2738 2·2789	2·2806 2·2857	0·2577 0·2586	2·0229 2·0271
	Mean $S_c = 2·0265$,		$h = 0·0370$,		$k = 0·00105$.	

STRAIGHT Vacuum Calorimeter, No. 1. D = 10·8 cm.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
1913. March 18	8·653 8·642	0·7816 0·7820	2·0343 2·0341	2·0462 2·0460	0·0223	2·0239 2·0237
March 31	8·482 8·480	0·8171 0·8163	2·0346 2·0356	2·0441 2·0451	0·0212	2·0229 2·0239
April 3	7·838 7·834	0·8111 0·8111	2·0368 2·0361	2·0439 2·0432	0·0214	2·0225 2·0218
April 3	7·921 7·917	0·8160 0·8161	2·0369 2·0362	2·0439 2·0432	0·0212	2·0227 2·0220
March 18	8·511	0·3855	2·0677	2·0794	0·0525	2·0269
March 31	8·282 8·286	0·3919 0·3916	2·0640 2·0642	2·0735 2·0737	0·0515	2·0220 2·0222
April 3	7·794 7·786	0·3915 0·3916	2·0661 2·0664	2·0736 2·0739	0·0515	2·0221 2·0224
March 18	8·585 8·578	0·1819 0·1818	2·1547 2·1561	2·1669 2·1683	0·1449	2·0220 2·0234
March 31	8·328 8·331	0·1839 0·1837	2·1604 2·1598	2·1702 2·1696	0·1425 0·1428	2·0277 2·0268
April 3	7·707 7·700	0·1853 0·1848	2·1549 2·1608	2·1625 2·1684	0·1409 0·1415	2·0216 2·0269
	Mean S_c = 2·0235,		h = 0·0148,		k = 0·00210.	

Same Calorimeter. D = 15·3 cm.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
April 7	8·159 8·157	0·7602 0·7598	2·0541 2·0556	2·0626 2·0641	0·0411	2·0213 2·0230
April 8	7·588 7·586	0·7796 0·7794	2·0572 2·0565	2·0640 2·0633	0·0400	2·0240 2·0233
April 9	7·438 7·429	0·8039 0·8037	2·0523 2·0531	2·0585 2·0593	0·0387	2·0198 2·0206
April 14	7·458 7·449	0·8063 0·8062	2·0527 2·0541	2·0595 2·0609	0·0386	2·0209 2·0223
April 7	8·084 8·084	0·3877 0·3875	2·0979 2·0990	2·1069 2·1080	0·0872	2·0197 2·0208
April 9	7·452 7·441	0·3903 0·3904	2·1044 2·1054	2·1110 2·1120	0·0866	2·0244 2·0254
April 14	7·455 7·449	0·3920 0·3921	2·1001 2·1016	2·1070 2·1085	0·0861	2·0209 2·0224
April 8	7·640 7·638	0·1814 0·1815	2·2357 2·2343	2·2431 2·2417	0·2196	2·0235 2·0221
April 9	7·437 7·439	0·1843 0·1842	2·2290 2·2285	2·2358 2·2353	0·2151	2·0207 2·0202
April 14	7·467 7·467	0·1812 0·1810	2·2336 2·2354	2·2409 2·2427	0·2199 0·2201	2·0210 2·0226
	Mean S_c = 2·0220,		h = 0·0285,		k = 0·00206.	

STRAIGHT Vacuum Calorimeter, No. 2. D = 13 cm. (approximately).

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
1913. June 30	7·076	0·7790	2·0560	2·0612	0·0383	2·0229
	7·078	0·7785	2·0556	2·0608		2·0225
July 3	7·203	0·7644	2·0568	2·0636	0·0391	2·0245
	7·201	0·7642	2·0560	2·0628		2·0237
June 28	7·032	0·3885	2·1032	2·1090	0·0835	2·0255
	7·040	0·3882	2·1006	2·1064		2·0229
June 30	7·028	0·3888	2·1043	2·1097	0·0833	2·0264
	7·032	0·3891	2·1007	2·1061		2·0228
July 3	7·043	0·3867	2·1008	2·1074	0·0839	2·0235
	7·043	0·3872	2·0968	2·1034		2·0195
June 30	7·077	0·1800	2·2337	2·2392	0·2141	2·0251
	7·077	0·1803	2·2324	2·2379	0·2137	2·0242
July 3	7·105	0·1806	2·2275	2·2345	0·2131	2·0214
	7·105	0·1804	2·2296	2·2366	0·2135	2·0231
	Mean S_c = 2·0235,		h = 0·0272,		k = 0·00204.	

Silica Calorimeter. Black Vacuum. D = 9·0 cm.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
1914. February 25	8·810	0·7758	2·0261	2·0354	0·0044	2·0310
	8·808	0·7759	2·0255	2·0348		2·0304
February 26	8·741	0·8048	2·0233	2·0318	0·0042	2·0276
	8·741	0·8045	2·0233	2·0318		2·0276
March 2	8·286	0·8119	2·0231	2·0308	0·0042	2·0266
	8·277	0·8111	2·0247	2·0324		2·0282
February 25	8·851	0·3760	2·0305	2·0401	0·0101	2·0300
	8·849	0·3760	2·0299	2·0395		2·0294
February 26	8·708	0·3768	2·0312	2·0401	0·0101	2·0300
	8·712	0·3766	2·0303	2·0392		2·0291
February 25	8·831	0·1770	2·0465	2·0562	0·0265	2·0297
	8·831	0·1772	2·0435	2·0532		2·0267
February 26	8·676	0·1800	2·0463	2·0554	0·0259	2·0295
	8·672	0·1803	2·0431	2·0522		2·0263
	Mean S_c = 2·0287,		h = 0·0030,		k = 0·00030.	

SILICA Calorimeter. Pressure in jacket about 1 mm. D = 9·0 cm.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
1914. March 2	8·504	0·8002	2·0187	2·0265	0·0136	2·0129
	8·502	0·8002	2·0179	2·0257		2·0121
	8·506	0·8006	2·0153	2·0231		2·0095
	8·518	0·3782	2·0447	2·0529	0·0430	2·0099
	8·512	0·3779	2·0464	2·0546		2·0116
	8·539	0·1793	2·1576	2·1659	0·1544	2·0115
	8·533	0·1793	2·1581	2·1664		2·0120
	Mean S_c = 2·0114,		h = 0·00600,		k = 0·00390.	

Silica Calorimeter. Black Vacuum. D = 12·5 cm.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
March 5	8·482	0·7999	2·0243	2·0348	0·0061	2·0287
	8·467	0·7995	2·0244	2·0349		2·0288
March 7	8·562	0·8201	2·0209	2·0312	0·0060	2·0252
	8·558	0·8198	2·0215	2·0318		2·0258
March 18	7·184	0·7990	2·0243	2·0346	0·0061	2·0285
	7·178	0·7986	2·0251	2·0354		2·0293
March 5	8·542	0·3778	2·0305	2·0405	0·0140	2·0265
	8·540	0·3773	2·0319	2·0419		2·0279
March 7	8·601	0·3806	2·0336	2·0441	0·0139	2·0302
	8·595	0·3807	2·0331	2·0436		2·0297
March 9	7·180	0·3808	2·0312	2·0416	0·0139	2·0277
	7·171	0·3811	2·0310	2·0414		2·0275
March 18	8·481	0·3775	2·0314	2·0435	0·0140	2·0295
	8·475	0·3768	2·0301	2·0422		2·0282
March 5	8·598	0·1764	2·0514	2·0621	0·0351	2·0270
	8·600	0·1761	2·0536	2·0643		2·0292
March 7	8·652	0·1756	2·0573	2·0680	0·0353	2·0327
	8·641	0·1761	2·0533	2·0640		2·0287
March 18	8·367	0·1749	2·0526	2·0647	0·0355	2·0292
	8·367	0·1749	2·0515	2·0636		2·0281
	Mean S_c = 2·0284,		h = 0·0045,		k = 0·00030.	

SILICA Calorimeter. Black Vacuum. D = 16·0 cm.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
1914. March 21	6·804	0·7862	2·0287	2·0390	0·0102	2·0288
	6·795	0·7867	2·0295	2·0398		2·0296
March 28	8·217	0·8051	2·0325	2·0401	0·0100	2·0301
	8·206	0·8051	2·0325	2·0401		2·0301
March 21	6·713	0·3773	2·0390	2·0500	0·0223	2·0277
	6·711	0·3772	2·0391	2·0501		2·0278
March 26*	7·258	0·3663	2·0345	2·0458	0·0229	2·0229
	7·254	0·3663	2·0355	2·0468		2·0239
March 28	9·083	0·3731	2·0433	2·0519	0·0226	2·0283
	9·077	0·3732	2·0428	2·0504		2·0278
March 23	7·129	0·1792	2·0801	2·0900	0·0519	2·0381
	7·136	0·1788	2·0732	2·0831		2·0312
March 28	9·233	0·1748	2·0738	2·0831	0·0531	2·0300
	9·235	0·1747	2·0738	2·0831		2·0300

Mean S_c = 2·0290, h = 0·0076, k = 0·00030.

Silica Calorimeter. Pressure in jacket about 1 mm. D = 16·0 cm.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
March 30	8·327	0·7853	2·0627	2·0700	0·0612	2·0088
	8·316	0·7855	2·0615	2·0688		2·0076
April 2	8·360	0·7873	2·0626	2·0710	0·0611	2·0099
	8·341	0·7866	2·0649	2·0733		2·0122
April 3	8·569	0·8081	2·0633	2·0714	0·0593	2·0121
	8·547	0·8080	2.0628	2·0709		2·0116
April 6	8·665	0·7908	2·0572	2·0677	0·0607	2·0070
	8·663	0·7908	2·0564	2·0669		2·0062
March 30	8·132	0·3782	2·1419	2·1493	0·1429	2·0064
	8·128	0·3778	2·1428	2·1502		2·0073
April 6	9·005	0·3547	2·1580	2·1692	0·1542	2·0150
	9·007	0·3550	2·1565	2·1677		2·0135
March 30	8·025	0·1768	2·3840	2·3914	0·3783	2·0131
	8·021	0·1769	2·3821	2·3895		2·0112
April 3	8·573	0·1816	2·3666	2·3751	0·3655	2·0096
	8·542	0·1819	2·3637	2·3722		2·0067
April 6	8·997	0·1751	2·3854	2·3967	0·3837	2·0130
	8·989	0·1756	2·3795	2·3908		2·0071
	8·978	0·1753	2·3853	2·3966		2·0129

Mean S_c = 2·0101, h = 0·0425, k = 0·00435.

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* Vacuum deteriorated.

Silica Calorimeter. Pressure in jacket about 1 mm. D = 9·0 cm.

(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
1914. April 24	9·086	0·8257	2·0206	2·0280	0·0169	2·0111
	9·082	0·8261	2·0206	2·0280		2·0111
	9·075	0·3566	2·0624	2·0698	0·0589	2·0109
	9·069	0·3566	2·0634	2·0708		2·0119
	9·196	0·1755	2·1967	2·2045	0·1943	2·0102
	9·192	0·1751	2·2020	2·2098		2·0155
	Mean S_c = 2·0118,		h = 0·0085,		k = 0·0045.	

Silica Calorimeter. Pressure in jacket 760 mm. D = 9·0 cm.

April 27	9·170	0·8467	2·0189	2·0256	0·0184	2·0072
	9·170	0·8465	2·0189	2·0256		2·0072
April 28	8·800	0·8144	2·0240	2·0311	0·0195	2·0116
	8·809	0·8132	2·0245	2·0316		2·0121
	8·813	0·8129	2·0238	2·0309		2·0114
April 30	8·706	0·8094	2·0223	2·0308	0·0196	2·0112
	8·714	0·8098	2·0192	2·0277		2·0081
	8·727	0·8081	2·0200	2·0285		2·0089
April 27	9·245	0·3569	2·0672	2·0739	0·0634	2·0105
	9·247	0·3570	2·0662	2·0729		2·0095
April 28	8·785	0·3792	2·0628	2·0698	0·0580	2·0118
	8·785	0·3788	2·0642	2·0712		2·0132
April 30	8·583	0·3768	2·0568	2·0655	0·0582	2·0073
	8·591	0·3765	2·0565	3·0652		2·0070
April 27	9·054	0·1780	2·2025	2·2094	0·1961	2·0133
	9·052	0·1779	2·2043	2·2112		2·0151
April 28	8·814	0·1781	2·1935	2·2011	0·1961	2·0050
	8·816	0·1780	2·1935	2·2011		2·0050
April 30	8·742	0·1780	2·1966	2·2056	0·1961	2·0095
	8·742	0·1780	2·1958	2·2048		2·0087
	Mean S_c = 2·0097,		h = 0·0105,		k = 0·00435.	

Silica Calorimeter. Black Vacuum. D = 9·0 cm.

May 1	8·603	0·7903	2·0298	2·0365	0·0062	2·0303
	8·597	0·7902	2·0309	2·0376		2·0314
	8·601	0·7902	2·0295	2·0362		2·0300
	8·590	0·3778	2·0368	2·0440	0·0140	2·0300
	8·588	0·3780	2·0351	2·0423		2·0283
	8·884	0·1785	2·0562	2·0639	0·0346	2·0293
	8·884	0·1785	2·0562	2·0639		2·0293
	Mean S_c = 2·0298,		h = 0·0045,		k = 0·00030.	

Summary of the Results.

The following table has been drawn up to show how the observed values of S_c, h, and k vary with the experimental conditions. In column (2) the calorimetric arrangement is briefly described. The dates in column (1) show the period of time over which the experiments with each calorimetric arrangement extended. Columns (3), (6), and (7) give the values of S_c, h, and k. The total number of observations giving the mean value S_c is stated in column (4). In column (5) are the distances D separating the middle of the thermometer bulb from the end of the heating coil. The last two columns give the value of the heat-loss per deg. per cm. (8), and the ratio of this quantity to k (9).

(1.)	(2.)	(3.) S_c.	(4.)	(5.) D.	(6.) h.	(7.) k.	(8.)	(9.)
1912. April to June	Non-vacuum and non-silvered jacket	2·0145	15	6·2	0·0033	0·00520	0·0074	1·4
		2·0147	13	8·7	0·0172	0·00520		
		2·0143	14	11·5	0·0400 (0·0390)	0·00520 (0·00538)		
		2·0135	19	13·8	0·0569	0·00520		
1912. Nov. to Dec.	Spiral flow-tube with silvered jacket	2·0265	20	—	0·0370	0·00105		
1913. March to April	Straight flow-tube with silvered vacuum jacket, No. 1	2·0235	19	10·8	0·0148	0·00210	0·0030	$1{\cdot}4_5$
		2·0220	20	15·3	0·0285	0·00206		
June to July	Ditto, No. 2	2·0235	14	13·0	0·0272	0·00204		
1914. Feb. to May	Silica flow-tube, silvered non-vacuum	2·0097	20	9·0	0·0105	0·00435		
	Pressure in jacket about 1 mm.	2·0116	13	9·0	0·0072	0·00420	0·0051	1·2
		2·0101	19	16·0	0·0425	0·00435		
	Black vacuum	2·0287	14	9·0	0·0030	0·00030	$0{\cdot}0006_5$	2·2
		2·0284	20	12·5	0·0045	0·00030		
		2·0290	14	16·0	0·0076	0·00030		
		2·0298	7	9·0	0·0045	0·00030		

Extrapolated value for the specific heat S_c at 104·5° C. and 760 mm., corresponding to zero heat-loss = 2·0300 joules per gr. deg. C.

With any definite calorimetric arrangement the values of S_c and k are constant within the limits of experimental error, while h increases linearly with D, fig. 10. In the set of experiments made with the non-vacuum jacket the values of h and k calculated in the manner described on p. 419 are given in the table in brackets. The most probable value of k, viz., 0·00520, has been used in the determination of H in the abridged tables, h being slightly altered in the case of the experiments with D = 11·5 cm. In the experiments made with the silica calorimeter, with as perfect a vacuum as possible in the jacket, the values of k calculated from the individual measurements varied between −0·0001 and 0·0007, and in the calculation of H/Q for these observations the mean value 0·00030 has been given to k.

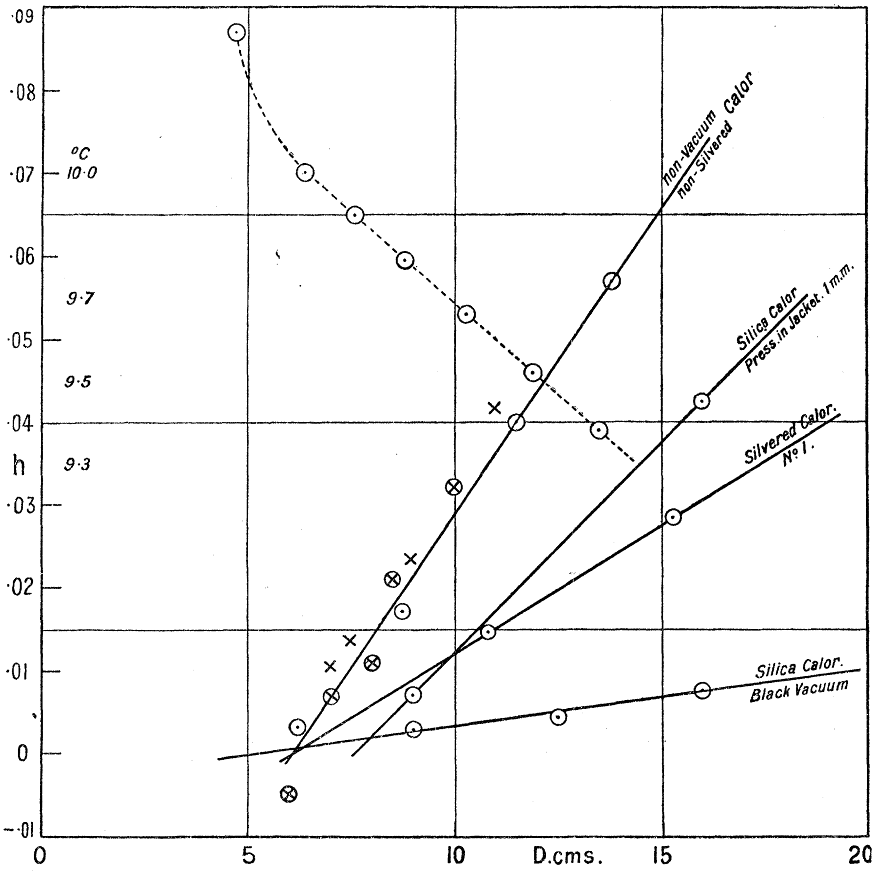

Fig. 10.

× Prof. Callendar's experimental values. Unsilvered calorimeters.

⊗ " " " Silvered "

⊙ Brinkworth. Mean values.

From the observations of May 1st, 1914, it can be seen that the difference in the values of the specific heats as calculated (1) from the experimental values of h and k, and (2) from the adjusted value of h corresponding to k = 0·00030, is only 0·05 per cent. In the last column of the above table are given the values of the ratio h per cm/k. Within the limits of error this ratio may be considered constant, and probably of the order 1·5. The two values of this ratio obtained with the silica jacket are not reliable, since in the case of the value 2·2 when $k = 0·00030$, a change in k of 100 per cent. will only cause the value of h/cm to be altered slightly, while when $h/cm/k = 1·2$ the experiments were carried out with a partial vacuum in the jacket, and there is a likelihood that the vacuum was not exactly the same throughout the period of these experiments, though practically constant for all the experiments made on one day.

Discussion of the Observed Variation of the Heat-loss with the Flow.

After completing the experiments with the non-vacuum jacketed calorimeter, the actual temperature gradients in the flow-tube, both when "hot" and when "cold," were observed in the case of each flow. The supply of electrical energy was adjusted so that with a distance of about 14 cm. between the end of the heating coil and the thermometer the latter indicated an outflow temperature about 9·3° C. above the cold temperature. The curves showing the temperatures at various points along the flow-tube are straight lines, provided that these temperatures are measured with the middle of the thermometer, not nearer than 6 cm. nor farther away than 16 cm. from the end of the heating coil. The actual gradients for the maximum, medium and minimum flows were of the order 0·044°, 0·090°, and 0·170° per cm., but it is necessary to point out that the third figure, though given, is not to be relied upon since the total fall of temperature is so small, only amounting to 0·35° C. over a distance of 8 cm. in the case of the maximum flow. The product of the temperature gradient over the straight line part of the curve and the value of the corresponding flow is in each case about 0·033. This number when multiplied by the specific heat and the product divided by the mean temperature of the flow-tube, gives 0·0072, a number which represents the heat-loss per cm. per degree and which is in good agreement with that deduced from the results of the calorimetric experiments, 0·0074. The gradient for a medium flow of 0·365 gr./sec. is shown in fig. 10 (dotted curve.) Another point worthy of notice is that the gradient ceases to be linear in that part of the flow-tube near the heating coil, and the shortest distance which must exist between the heating coil and the thermometer in order to obtain complete mixing, is indicated, both in the gradient observations and in the calorimetric experiments, to be about 6 cm. The agreement between the values of h/cm, calculated from the calorimetric experiments and from the gradient observations in the lower part of the flow-tube, indicates that the k/Q term in the heat-loss represents the loss from the upper portion of the flow-tube. A possible explanation of this is as follows. The steam in the flow-tube loses heat to the upward current surrounding it, and heat is lost from this upward current to the surrounding brass jacket. However, it is only the heat given to the jacket which is *actually* lost. The heat lost from the steam in the flow-tube to the up-current is proportional to the rise of temperature $d\theta$. The temperature of the up-current is consequently raised by an amount proportional to $d\theta/Q$, so the *actual* loss to the jacket is $k^1\,d\theta/\mathrm{Q}$, where k^1 is some constant. If, on the other hand, there had been no counter current, the heat-loss would have been due to radiation alone and would have been represented by a term $h\,d\theta$. With the counter current there will still be radiation, and the term representing the *total* heat-loss will be of the form $(h+k/\mathrm{Q})\,d\theta$. If we assume that the heat-loss $h_1\,d\theta$, by direct radiation from the upper part of the flow-tube to the jacket, is of the same order as that fraction of the heat-loss $h_2\,d\theta$ gained by the up-current from the lower part of the flow-tube, which is returned *into* the flow-tube, and if this equivalence exists when the upper part of the flow-tube includes a length extending to 6 cm. below the heating coil, the $h\,d\theta$ term will represent the *total direct radiation loss* from the lower part of the flow-tube to the jacket, and the $k/\mathrm{Q}\,d\theta$ term, the heat lost from the upper part of the flow-tube to the jacket. If this assumption is correct we should expect to find k constant in all the experiments made with a definite calorimetric arrangement; moreover, k should be proportional to the value of the heat-loss per centimetre. Since the thermal exchanges which occur between the two currents of steam, and between these and the outer brass jacket, are undoubtedly very complex, the above explanation must only be considered as approximately describing what is taking place. It has been put forward mainly in order to justify, to some extent, the adoption of the type of equation used in the calculations. The values of S_c obtained show a distinct variation with the magnitude of k, *i.e.*, with the value of the heat-loss per degree per centimetre (fig. 11). The extrapolated value of the specific heat, corresponding to zero heat-loss, is only 0·05 per cent. higher than the mean deduced from the results obtained under the best experimental conditions, hence this value has been taken as the final result of these experiments,

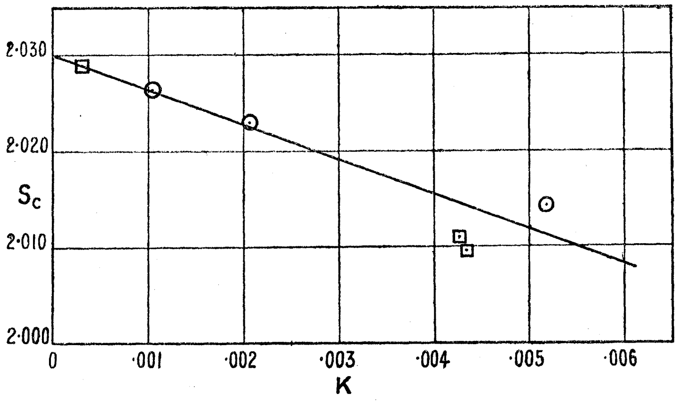

Fig. 11.

⊡ Silica calorimeter.

⊙ Other calorimeters.

$$\mathrm{S} = 2{\cdot}0300 \text{ joules per gr. deg. at } 104{\cdot}5^\circ \text{ C.}$$
$$\mathrm{S} = 0{\cdot}4856 \text{ calories per gr. deg. at } 104{\cdot}5^\circ \text{ C.},$$

this latter result being in terms of the calorie at 20° C.

Comparison of the Result with Theory.

The values of the specific heat at constant pressure can be deduced from equation (7), and this relation has been used in order to compare my value of the specific heat with values obtained by other observers. Assuming the linear variation with temperature, as experimentally determined, my own observations give the value 0·4878 as the specific heat at 100° C. Substituting this value in the above equation we find $S_0 = 0·4634$.

The values of the specific heat at atmospheric pressure and at various temperatures can then be calculated and the mean value over any desired range deduced. Over the range 110° C. to 230° C. the mean value is thus found to be 0·476. From equation (5) the following expression showing the variation in the total heat of steam can be derived

$$F - F_0 = S_0(\theta - \theta_0) - (n+1)(cp - c_0 p_0) + b(p - p_0).$$

Assuming 640·3 calories as the value of the total heat at 100° C. we find the latent heat at 0° C. to be 596·7 cal./gr. which is in good agreement with that found by DIETERICI. The above values of S_0 and L_0 may be used to calculate the saturation pressures of steam. The agreement found between the calculated values and those determined experimentally is exceedingly good, especially at low temperatures when the value of S_0 is approximately constant. For example, the calculated pressures at 0° C. and at 60° C. are 4·585 mm. and 149·23 mm. respectively, the experimental values at these temperatures are at 0° C. 4·600 mm. (REGNAULT) and at 60° C. 148·80 mm. (REGNAULT).

Comparison of this Result with the Work of other Observers.

On pp. 397–399, Prof. CALLENDAR has discussed the work of other observers. The value of the specific heat at 108° C. deduced from my experimental measurements is 2·0230 or 0·484 with the calorie as the unit.

In fig. 10 I have plotted the values of h obtained by Prof. CALLENDAR against the corresponding values of D. The points line about a straight line which practically coincides with that obtained from my measurements with the non-vacuum, non-silvered calorimeter. Apparently there is no systematic difference in the values of h/cm obtained with the silvered and unsilvered calorimeters respectively. When considered, together with the results of my own experiments with various pressures in the vacuum jacket, this concordance indicates that in the many calorimeters, evacuated by the makers, which have been used, the vacua produced were far from perfect. It is again of interest to note that in Prof. CALLENDAR's experiments similar absurdly low values of the specific heat were obtained when attempts were made to mix the steam by means of wire gauze.