PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

On the Specific Heats of Air and Carbon Dioxide at Atmospheric Pressure by the Continuous Electric Method at 20 degrees C. and 100 degrees C.

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Phil. Trans. R. Soc. Lond. A 1911 **210**, 199-238
doi: 10.1098/rsta.1911.0006

VI. *On the Specific Heats of Air and Carbon Dioxide at Atmospheric Pressure by the Continuous Electric Method at* 20° *C. and* 100° *C.*

(*Experiments performed in the Physical Laboratory of the Royal College of Science, London, S.W.*)

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Received October 8,—Read December 10, 1908,—Received in condensed form November 13, 1909.

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(1) INTRODUCTION.—The first reliable investigation of the specific heats of gases was made by REGNAULT,[*] who in an elaborate series of experiments measured the specific heats of several gases at constant pressure by the method of mixtures. This method, which in modified forms has been employed by nearly all subsequent observers, presents great difficulties when applied to gases, and further, it only gives the mean values of the specific heats over large ranges of temperature, and it is consequently not well adapted to the detection of small variations of the specific heat with temperature. During the period in which I was at the Royal College of Science, London, Prof. CALLENDAR suggested that I should make some measurements of the specific heats of air and carbon dioxide by the continuous electric method, which is particularly well adapted to the measurements of specific heats over small ranges of temperature. I should like to take this opportunity of expressing my deepest thanks to Prof. CALLENDAR for his advice and encouragement throughout the work.

(2) *Outline of the Method.*—A constant stream of gas is passed through a tube GF, fig. 1, to be presently described, into a jacket J, which surrounds a central tube AB. The gas passes into the tube AB at the temperature of the jacket, and is there heated by an electric current passing through a platinum coil P, the rise in temperature being measured by two platinum thermometers, K and H, used differentially.

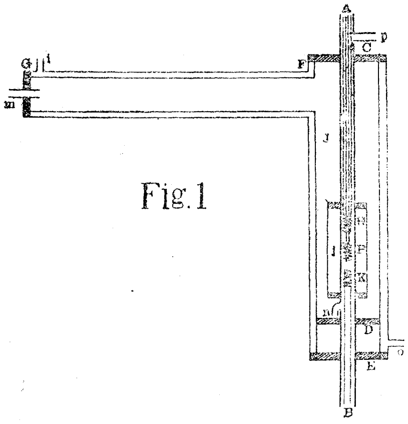

Fig.1

If C is the electric current, E the potential difference between the ends of the heating coil, Q the mass of gas which flows through the apparatus per second, $\delta\theta$ the rise in temperature of the gas, J the mechanical equivalent of heat, and S the specific heat of the gas at constant pressure, then neglecting for the present the heating effect of the leads of the heating coil, we have, when the temperature conditions of the different parts of the apparatus have become steady,

$$\mathrm{CE} = \mathrm{JSQ}\,\delta\theta + h\,\delta\theta, \quad \ldots\ldots\ldots \quad (1)$$

where $h\,\delta\theta$ is a term representing the heat loss. If now the rate of flow of the gas is

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[*] 'Memoires de L'Academie des Sciences de L'Institut Imperial de France,' 1862.

altered to about half its original value, and if the electric current is adjusted so that the rise in temperature of the gas is the same as before,

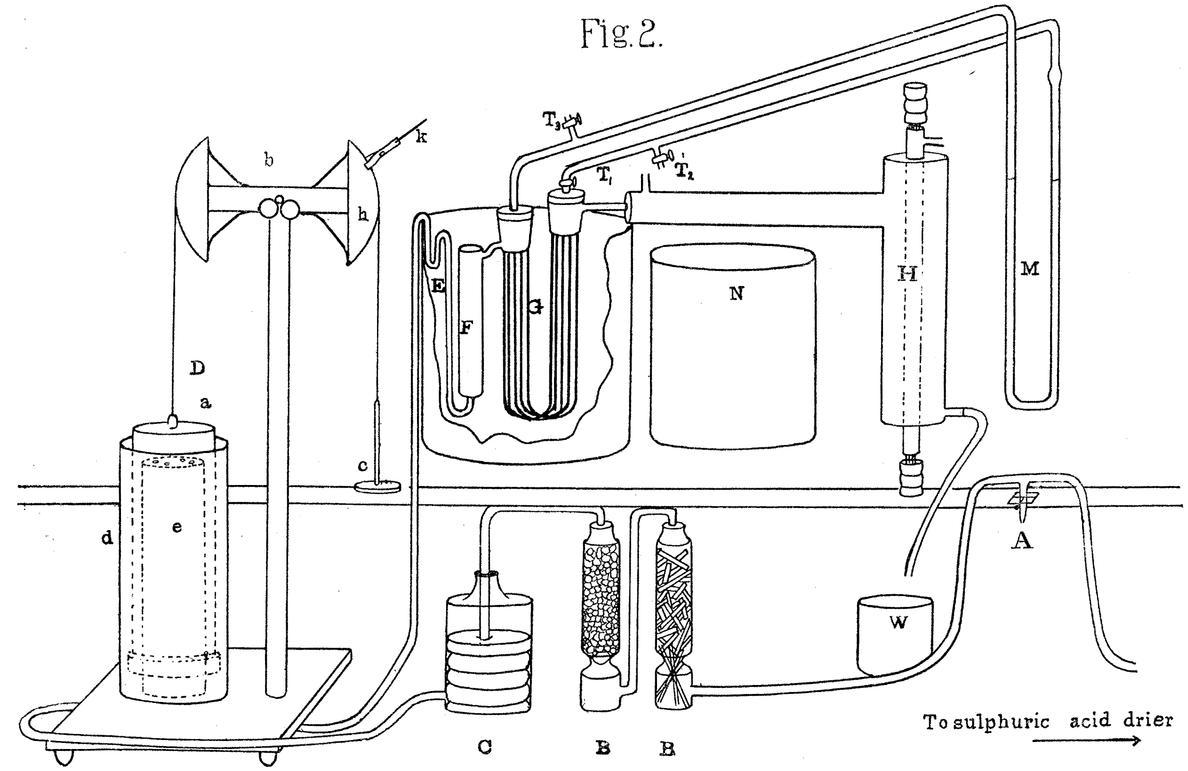
$$C_1E_1 = JSQ_1\,\delta\theta + h\,\delta\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

where the letters with suffixes refer to the new values of the corresponding quantities in (1). From (1) and (2) h may be eliminated, leaving an expression for S which does not involve the heat loss.

The rates of flow of the gas were obtained by passing it through sixteen fine metal tubes arranged in parallel, and measuring the pressure difference between their ends, the absolute pressure at one end, and their temperature. The expression giving the rates of flow in terms of these quantities was obtained from the results of a separate series of experiments.

In the experiments on the specific heat of air the gas was pumped continually through the apparatus by a bellows, worked by an adjustable crank driven by a wheel which was connected to a motor. This part of the apparatus was placed at the far end of the room, and the motor was turned in such a direction that it did not affect the needle of the galvanometer which was used with the platinum thermometers. The gas passed from the bellows to a sulphuric acid dryer, consisting of a wide glass tube about 1 metre long, half filled with pure strong sulphuric acid, and strapped to a board which was fixed to the floor by two brass springs, so that the tube could rock parallel to its axis. The rocking caused a constant renewal of the surface of the acid, and was brought about by connecting the board by means of a steel wire to the top of the bellows. The acid was renewed daily during the experiments. The gas passed from the sulphuric acid dryer into a Wolff's bottle, which served to collect any sulphuric acid spray, and thence to the towers BB, fig. 2, through a piece of composition tubing and the T-piece A, which was open to the atmosphere through a piece of rubber tubing partially constricted by a clip. The flow of the gas through the apparatus could be roughly adjusted by allowing some of it to escape into the atmosphere. The first of the towers BB contained solid KOH to remove any carbon dioxide, sulphuric acid, or water vapour remaining in the gas, and the second contained calcium chloride. The gas passed from the towers through a cotton wool dust filter C to an automatic pressure regulator D, to be presently described; from D it passed through the throttles E into a wide brass tube F, packed with copper gauze, in which it accurately took up the temperature of the surrounding bath before entering the fine metal tubes G, from which it passed through the calorimeter H into the atmosphere. M represents the oil gauge, with which were associated the glass taps $T_1T_2T_3$, to which further reference will be made. The tank N contained water, which in the experiments at the temperature of the room was siphoned round the jacket of the calorimeter into the vessel W, from which it was poured back again into N.

Fig. 2.



The larger rates of flow amounted to about 0·5 litre per second, for, unless the rate of flow is fairly large, the heat loss, which depends upon the temperature rise and not upon the flow, forms an appreciable percentage of the whole energy supplied.

(3) *Measurement of the Electrical Energy.*—The electric current was supplied by four large accumulators. It passed through a rheostat, the heating coil of the calorimeter, and a standard resistance coil which will be referred to as the secondary standard. If E_1 and E_2 are the potential differences between the ends of the heating coil and standard resistance coil respectively, and if R is the resistance of the standard, the electric energy supplied to the heating coil per second is E_1E_2/R.

E_1 and E_2 were measured in terms of the cadmium cell, on a four-dial potentiometer. The potential differences between the ends of either the heating coil, standard coil, or cadmium cells could be balanced on the potentiometer by bringing the leads to six mercury cups, cut in a paraffin block in the manner indicated in fig. 3.

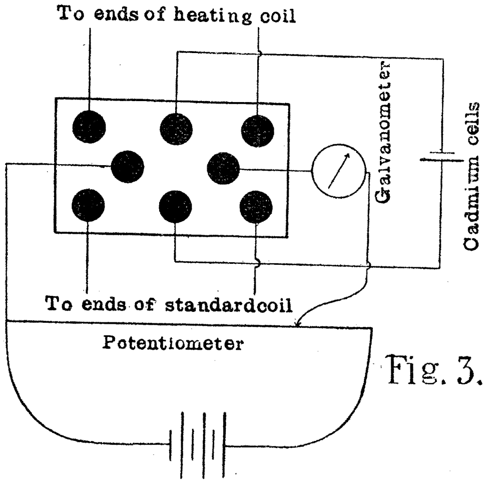


Fig. 3.

DETAILS OF THE APPARATUS.

(4) *The Continuous Flow Electrical Calorimeter.*—The calorimeter is represented diagrammatically in fig. 1. The tube AB, which may be termed the calorimeter proper, consisted of a glass tube about 60 cm. long, the space containing the platinum thermometers and heating coil being surrounded by a glass jacket *j*. The calorimeter proper was fixed by rubber corks C, D, E, into a double-walled vessel, 44 cm. long and 5 cm. internal diameter, which was continued into a double-walled tube FG, packed with tightly-fitting discs of copper gauze. The tube FG formed the heater in which the gas attained the desired temperature. The whole double-walled vessel thus consisted of two L-shaped vessels, one inside the other, the ends of the annular spaces between the double walls being closed with tightly-fitting brass rings soldered in. The space between the double walls was provided with an inlet (*i*) and an outlet (*o*), so that water or steam could be passed round the apparatus for the purpose of keeping it at a constant temperature. The gas under investigation entered by the tube *m*, passed through the tightly-packed gauze in GF, where it took up the required temperature, and entered the space round the calorimeter proper; it next passed through the tube *n* into the calorimeter proper, and finally emerged by the tube *p*. The ends of AB were closed by the rubber corks through which the platinum thermometers and heating coil leads passed.

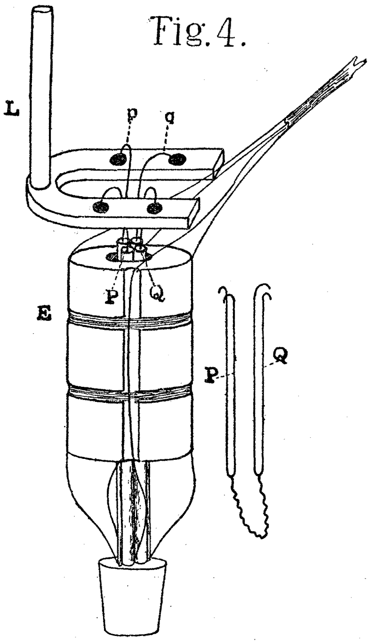
The above method of heating the gas was found to be most efficient; a thermometer placed in the exit end of the calorimeter proper recorded 99°·9 C., while the same thermometer placed in the steam recorded 100° C. The essential requirement was not that the temperature of the gas should be exactly equal to that of the steam, but that it should remain constant, and this was found to be the case to a surprisingly high order of accuracy, the temperature remaining steady often to 0°·01 C. for two or three hours, allowance being made for fluctuations in atmospheric pressure. The function of the cork D was to prevent the gas becoming cooled by impinging on the cork E, which was in direct contact with the atmosphere. A slight cooling effect, due to the gas impinging on C, was of little consequence, since it became warmed again in its passage down the jacket of the calorimeter proper, and it was the temperature of this gas which determined the temperature of the jacket *j*. All that was essential was that the gas should enter the calorimeter proper at the temperature of the jacket *j*. The parts of the leads which were contained in that portion of the calorimeter proper, which projected outside the jacket, were lagged with cotton wool in order to reduce the temperature gradient in them, and consequently the conduction of heat from the gas.

(5) *The Platinum Thermometers and Heating Coil.*—The platinum thermometers and heating coil were wound on three serrated mica frames. The heating coil leads were four in number, two for carrying the current, and two for connection to the potentiometer. Each current lead was connected to its potential lead by a piece

of thick platinum wire, which was fused into two thin glass tubes, one surrounding each of the leads. The glass tubes were brought side by side, and made to grip one of the mica frames. A length of about 100 cm. of 0·008-inch pure platinum wire was bent double, and the loop end was gold-soldered to the junction of a current and a potential lead. The two strands were wound in parallel on the mica frame, the free ends being gold-soldered to a piece of thick platinum wire, which was passed up the frame, and was soldered to the junction of the other current and potential leads. The resistance of the coil so constructed was just over 1 ohm at the temperature of the room. A second mica frame was slid up between the glass tubes until its centre was about 8 cm. from that of the heating coil, and one of the platinum thermometers was wound on this frame from 0·004-inch pure platinum wire, the ends of its compensating leads being joined by a piece of the same platinum wire in the manner adopted by Prof. CALLENDAR for the compensation of the cooling effect of the leads on the thin thermometer wire. To insure insulation from the glass surfaces surrounding the heating coil leads, the thermometer leads were enclosed in fine glass tubes, the whole being bound firmly together with silk.

The thermometer above referred to served to measure the temperature of the gas after it had been heated by the electric current; it will be referred to as the thermometer H. The other thermometer K was wound in a similar manner. Several little discs of copper gauze were threaded between the heating coil and the thermometer H. These discs, in virtue of their high thermal conductivity, served to distribute the heat uniformly throughout the gas as it passed from the heating coil to the thermometer. The external thermometer leads were soldered to the internal leads, and were bound with insulating binding to ebonite heads, fig. 4, fixed firmly on the glass tubes which projected from the ends of the thermometers. The method adopted for connecting the internal and external current and potential leads is indicated in fig. 4. The four leads coming up through the hole in the ebonite head E are bent over, and dip into four mercury cups in an ebonite horse-shoe, which was supported from a clamp by the handle L; the external leads were brought to these mercury cups. This arrangement enabled the connections to the internal current and potential leads to be interchanged, to eliminate possible difference of exact similarity between them.

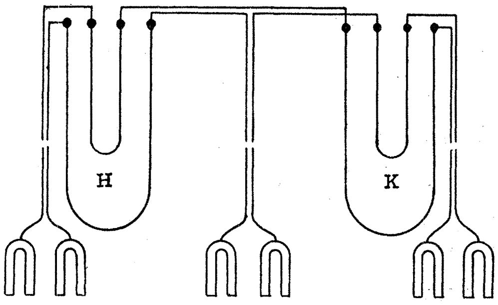
Fig. 4.



(6) *The Platinum Thermometer Bridge and the Measurement of the Fundamental Intervals.*—The bridge was of the well-known form designed by Prof. CALLENDAR, with mercury cups in place of plugs. Two calibrations of the coils and of the bridge wire were made, full details of which have been preserved. No two corresponding

readings in the two calibrations differed by an amount corresponding to as much as 0°·001 C. in the main experiments, and indeed the coils themselves were remarkably accurate, the average error amounting to less than 0·01 cm. of bridge wire. A movement of 10 cm. on the bridge wire corresponded to an alteration of 0·1 ohm in one of the arms of the bridge, or to an alteration of 2° C. in the temperature of one of the thermometers. The galvanometer used with the bridge was of the astatic type, with a quartz fibre suspension, and the sensitiveness in the main experiments was such that a movement of 0·1 mm. on the bridge wire caused an alteration of 10 divisions in the deflection on reversing the current. A reversing key was used in the battery circuit throughout, so that thermo-electric effects could be eliminated by balancing until there was no alteration of the galvanometer deflection on reversing the current.

Fig. 5.



The accompanying diagram, fig. 5, shows the arrangement of the thermometer leads, the leads which are drawn side by side being equal in resistance. H and K are the two platinum thermometers, the smaller loops representing the compensating portions. It will be seen that the arrangement of the leads is such that the thermometers can be joined up to the bridge either separately or differentially.

The usual apparatus was employed for the determination of the fixed points. Since it was on the thermometer H that the rise in temperature in the main experiments was measured, it was essential that this thermometer should be guarded against all possible sources of irregularity. The eight leads associated with this thermometer and the heating coil caused some difficulty at first in the accurate determination of the fundamental interval, since they tended to conduct heat away from the space surrounding the thermometer coil, but special precautions were taken which successfully eliminated this effect. It would have simplified matters if the heating coil had been wound on the prolongation of the axis of thermometer K, as H would then have had only four leads associated with it. Full details of the determinations of the fundamental intervals have been deposited in the archives of the Royal Society, but the following is a summary of the results :—

Thermometer H.

Experiment 1.	Fundamental Intervals	5·1910 ohms.
„ 2.	„ „	5·1920 „
„ 3.	„ „	5·1917 „
Mean	„ „	5·1916 „
Resistance at 0° C.	. . . .	13·3761 „

THERMOMETER K.

Experiment 1.	Fundamental Intervals	5·1454 ohms.
,, 2.	,, ,,	5·1445 ,,
,, 3.	,, ,,	5·1446 ,,
Mean	,, ,,	5·1450 ,,
Resistance at 0° C.		13·3039 ,,

The relationship between the temperatures t and t_{pt} on the absolute scale and on the platinum scale, respectively, can be expressed by the formula $t-t_{pt} = d\,.\,t\,(t-100)\,.\,10^{-4}$, where d is a constant which may be taken equal to 1·5 for pure platinum. This expression, combined with the above observations, enables the values of α and β in the expression $R_t = R_0\,(1+\alpha t+\beta t^2)$ to be calculated. The values for the thermometer K are $\alpha = 0{\cdot}0039253$, $\beta = -0{\cdot}000{,}000580$; and for the thermometer H, $\alpha = 0{\cdot}0039394$, $\beta = -0{\cdot}000{,}000582$.

The difference in the values of the coefficients is probably due to a difference in the treatment to which the thermometer wires were subjected in winding. It is satisfactory to observe that the higher coefficient is found in the thermometer H, in which we should expect the effect of thermal conduction through the leads to be the greater; this circumstance points to a true difference in the values of the coefficients.

Two pieces of solid caustic soda were placed in the bottoms of the tubes which held the thermometers during the determinations of the lower fixed points. The insulation of the thermometers was tested from time to time, and found to be almost perfect.

(7) *The Cadmium Cells.*—The cadmium cells were of the well-known H pattern. The amalgam contained 12·5 per cent. of cadmium, and was prepared electrolytically according to the specification given by F. E. SMITH ('B.A. Report,' South Africa, 1905). The mercurous sulphate and cadmium sulphate used were supplied by KAHLBAUM, the cadmium sulphate being recrystallised and tested in the manner described by SMITH. Four cells were made up, but only two of these cells, (2) and (3), were used in the work which follows. A comparison of these cells with a cell (7) made up two years previously showed that (2) and (3) were lower in E.M.F. than (7) by 0·00014 volt and 0·00012 volt respectively. At a later date these cells were sent to the National Physical Laboratory, where they were tested over a period of seven months. It was found that while cell (7) had remained practically constant, a slight fall was observed in the case of cells (2) and (3); this was immaterial, however, since the cells were compared with cell (7) during the actual research. The full data referring to the tests of the cells are preserved in the archives, the mean value for the cells (2) and (3) at the time when they were actually used in the calorimetric experiments being 1·01835 volts at 17° C. in terms of the international ohm and the ampere (10^{-1} C.G.S. unit). This value corrected to the temperature of the experiments has been taken for the calculation of the specific heats. That value, 4·180

Joules/cal. at 20° C., obtained by Barnes* for the mechanical equivalent of heat, corresponds to the international ohm, and to the value 1·4334 volts for the E.M.F. of the Clark cell at 15° C., this value for the Clark cell being obtained by direct measurement in terms of the international ohm and the ampere (10^{-1} C.G.S. unit).† Thus, by using the above value for the cadmium cell and taking the international ohm as the unit of resistance, the specific heats are expressed in terms of the calorie at 20° C., which is assumed to be equal to 4·180 Joules.

(8) *The Potentiometer.*—The potentiometer was of the form designed by Prof. Callendar. The principle involved is similar to that involved in the Thomson-Varley slide, but the instrument has four dials instead of two. The second dial could be made to form a shunt across any adjacent pair of coils of the first; the third dial was related in a similar way to the second, and the fourth to the third. The resistances of the coils in the different dials were so adjusted that the potentiometer read directly in a manner somewhat similar to the Thomson-Varley instrument; the thousands were read off on the first dial, the hundreds on the second, the tens on the third, and the units on the fourth. A full account of the details of the calibration of the instrument, together with the tables of observations, have been preserved, and since it can be shown from them that by no conceivable arrangement of the sliders can an error of as much as 1 part in 10,000 arise in the actual potentiometer readings through neglect of the calibration corrections, no corrections have been applied.

The current for the potentiometer was supplied by two freshly made up Leclanché cells. The galvanometer used was of the Thomson pattern; it had a resistance of 7000 ohms, and the sensitiveness in the main experiments was such that a change of unit amount in lowest dial of the potentiometer produced an alteration of 10 divisions in the deflection.

(9) *The Secondary Standard Resistance.*—The coil was wound on a wooden frame from about 50 cm. of No. 22 manganin wire, and it was placed in a double-walled vessel containing oil. Water from the tap passed through the space between the double walls, and the temperature could be measured by a thermometer passing through the lid and dipping into the oil. The ends of the coil were soldered to two thick copper U-pieces, the ends of which were connected to four brass terminals, two for the current leads and two for the potential leads. The secondary standard was compared with a primary standard 1 ohm coil by passing the same current through each, and comparing the potential differences between the ends of the coils on the potentiometer; thus, all question as to the resistances of the leads was avoided. The comparison having been made, the current of water passing through the jacket of the coil was stopped; the electric current was caused to flow through the secondary

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* 'Phil. Trans.,' A, 314 (1902).

† 'Phil. Trans.,' A, 313, p. 86 (1902).

standard alone until its temperature had risen about 5° C., this being about the maximum variation in temperature experienced by the coil during the research, and the coils were again compared. The results of several observations, full details of which have been preserved in the archives, lead to the expression $R = 1{\cdot}03899 + 0{\cdot}000084\,(t - 18{\cdot}7)$ ohms for the resistance of the secondary standard in terms of its temperature t.

(10) *The Pressure Regulator.*—The pressure regulator was of the form designed by Prof. Callendar. It consisted essentially of an inverted bell (a, fig. 2) weighted at the bottom, and suspended in oil by a steel tape from a wooden beam b, which was supported on friction wheels, and which formed one arm of a balance. From the other arm a support (c) for weights was hung by another steel tape. Gas could be blown into the bell either directly through pipes, or through the fixed inverted bell shown at e in the figure. So long as the suspended bell was floating the pressure of the gas inside it was constant, and independent of its degree of immersion, except to a very slight extent, owing to the buoyancy effect on the thin copper of which the bell was made. The buoyancy effect was easily overcome by attaching a clamp (κ) asymmetrically to one end (h) of the beam, and adjusting its asymmetry so as to automatically effect the compensation.

It was most essential that the oil should contain no volatile constituent. To test this point, the full current of gas was passed over a weighed quantity of oil for half an hour, and the oil was reweighed. In this way it was possible to form an estimate of the amount of evaporation which would take place in the bell. An evaporation of oil amounting to one part in 10^5 by weight of the total quantity of gas passing over the oil could easily have been detected, but no alteration in weight was found.

(11) *The Oil Gauge.*—The gauge which served to measure the pressure difference between the ends of the fine tubes contained Fleuss pump oil. It consisted of a U-tube graduated in millimetres on both limbs, and was fixed to a board which was clamped to a massive cast-iron support in order to keep it firmly fixed throughout the work. The fractions of a millimetre were obtained by two microscopes, with scales in the eye-pieces; by removing the front lenses of the objectives it was easy to place the microscopes so far away from the limbs of the gauge that the oil menisci and the graduations were in focus at the same time. The gauge graduations were carefully calibrated by means of a small cathetometer giving a fairly large magnification. Two calibrations were performed in which no two corresponding readings differed by more than 0·04 mm., and the agreement was generally to 0·02 mm. Full details of the calibrations have been preserved. In order to measure the pressure difference between the ends of the fine tubes, taps T_2 and T_3 (fig. 2) were closed, tap T_1 being open. By closing T_1 and T_3 and opening T_2 the excess pressure at the high-pressure ends of the tubes over that of the atmosphere was obtained. T_3 was to enable the pressure in the bell to be measured if required. The mean of the pressures at the two ends of the tubes was obtained by subtracting half the pressure difference between the ends from

this quantity, and adding the result, reduced to centimetres of mercury, to the atmospheric pressure.

The density of the oil was not of primary importance for deducing the rate of flow through the tubes, since the latter were calibrated with the pressure differences measured in centimetres of oil, an approximate knowledge of the density was however necessary in order to perform the reduction from oil pressure to mercury pressure mentioned above. A determination of the density and coefficient of expansion of the oil showed that if h_0 is the head in centimetres of mercury at 0° C. corresponding to the head h measured in centimetres of oil at t° C., the expression for h_0 is

$$h_0 = h\,(0{\cdot}0639)\,(1-0{\cdot}00076\,[t-22]).^*$$

The rather large variation of the density of the oil with temperature made it advisable to observe the temperature of the gauge after each set of readings, and it was also necessary to ensure equality in the temperature of the two limbs, since a difference in temperature of 0°·5 C. between them might cause an error of 2 parts in 1000 on a head of 10 cm. in a case where there were long lengths of column below the menisci in the two limbs. Errors of this kind are not systematic however, and the agreement of the final results is such as to show that they did not produce any serious effect. A source of error might be expected to be introduced if the gauge became tilted during the experiments; the effect of a tilt is to produce on the pressure readings a second order error varying as the cosine of the angle of tilt, and a first order error due to the elevation of the graduations on one limb and the depression of those on the other. The latter error becomes reduced to a second order one on the specific heat, however, in virtue of the method of calculating this quantity from two experiments with different flows of gas. It would be entirely eliminated if the flow were accurately proportional to the pressure difference between the ends of the fine tubes, for if x is the error in pressure due to tilt of the gauge, H the observed pressure, and A the constant by which the pressure must be multiplied in order to obtain the rate of flow, we have

$$C_1E_1/\delta\theta_1 = A\,(H_1+x)+h, \quad \text{and} \quad C_2E_2/\delta\theta_2 = A\,(H_2+x)+h,$$

where CE and $\delta\theta$ have the meanings assigned to them on p. 200. On subtracting the second equation from the first, it will be seen that x is eliminated just as h is eliminated. The level readings of the oil in the gauge were taken several times during the research, but the greatest variation amounted to only 0·06 mm., which is much too small to produce any appreciable error; even this variation may possibly have arisen from inequalities in temperature between the limbs of the gauge.

The oil was always drawn up so as to wet that portion of the gauge above the point at which it finally settled; it was rather sluggish in its movements, and readings

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* 22° C. is the temperature to which all the gauge readings were reduced.

could not be taken until it had all drained down the gauge. It was found, however, that when the oil had nearly settled down, two simultaneous readings on the two limbs gave the same pressure difference as when it had become quite stationary. In the experiments on carbon dioxide a device was adopted to shorten the time which the oil took to drain.

(12) *The Preliminary Experiments.*—A long series of preliminary experiments was performed for the purpose of testing the validity of the assumption made on p. 200 that the electrical energy supplied per unit rise in temperature bears a linear relationship to the rate of flow of the gas. It was first necessary to obtain an expression for the rate of flow in terms of the pressure difference between the ends of the tubes and the mean pressure in them, for on account of the inertia effects of the gas it was by no means proportional to the product of these quantities. All the tubes except one were blocked up; the pressure was blown up in the bell, and the latter was allowed to discharge gas through the fine tubes. The time taken for the bell to fall between two fixed marks (the cross wires of two fixed telescopes) was accurately noted, and the corresponding pressure readings were obtained. By performing a series of experiments of this kind with different rates of flow it was found that the rate of flow through the tube under examination was proportional to the quantity

$$\mathrm{F} = \{\sqrt{(1+0{\cdot}1043\mathrm{H})}-1\}\, P,$$

where H is the pressure difference between the ends of the tubes, and P the mean pressure in them. The rate of flow through all the tubes in parallel was assumed to be proportional to this quantity, this assumption being sufficiently accurate for the purpose in hand in the preliminary experiments. The variation of the rate of flow with the temperature of the tubes amounted to about 0·5 per cent. per degree, but it was measured and allowed for.

The method of performing the calorimetric experiments was almost exactly the same as that to be presently described for the final experiments. The following two tables represent the results of a typical series of preliminary experiments. Assuming a linear equation of the form $\mathrm{CE}/\delta\theta = \mathrm{AF}+h$, where A and h are constants, and the other quantities have the significance already assigned, the values of A and h which best satisfied the observations were found. The extent of the agreement will be seen from the tables. The heating effect of the leads was neglected in the preliminary experiments, for since it represents a practically constant fraction of the energy supplied in each flow, it does not appreciably destroy the linear relationship between $\mathrm{CE}/\delta\theta$ and F.

The errors in the third columns of each table are estimated as percentages on the energy supplied in the largest rate of flow. In the calculations several corrections which remain sensibly constant throughout the series of experiments, and therefore do not affect the linear relationship, have been omitted. The rise in temperature in the above experiments was about 5° C., but in order to test the method under conditions as varied as possible, an experiment was performed with a rise in temperature of 10° C., the results were found to be consistent with the above to 1 part in 1000.

ATMOSPHERIC Temperature.

Date.	CE observed.	CE calculated.	Error.
			per cent.
July 6	0·41822	0·41797	−0·03
	0·71283	0·71258	−0·03
	0·58428	0·58403	−0·03
„ 9	0·58629	0·58508	−0·16
	0·71333	0·71333	0·00
	0·46228	0·46319	+0·12
„ 10	0·46641	0·46536	−0·14
	0·58277	0·58226	−0·07
	0·74020	0·73985	−0·05
„ 11	0·74287	0·74308	+0·03
	0·43193	0·43203	+0·01

STEAM Temperature.

Date.	CE observed.	CE calculated.	Error.
			per cent.
June 27	0·70030	0·70030	0·00
	0·44090	0·44046	−0·06
	0·61713	0·61565	+0·20
„ 28	0·35409	0·35286	−0·17
July 2	0·36211	0·36201	+0·01
„ 3	0·35601	0·35881	+0·30
	0·45743	0·45857	+0·16
	0·65724	0·66019	+0·40
„ 4	0·70325	0·70178	−0·20
	0·42746	0·42776	+0·04
„ 10	0·36226	0·36152	−0·10
„ 11	0·44282	0·44159	−0·17
„ 12	0·71900	0·72033	+0·18
	0·44676	0·44646	−0·04

(13) *Theoretical Examination of the Variation of the Heat Loss with the Flow.**—The elementary theory given on pp. 200 and 201 involves the assumption that the heat loss for a given rise in temperature of the gas depends only upon that rise in temperature and is independent of the rate of flow, which is not strictly true, since the heat loss also varies with the form of the temperature curve between the heating coil and the thermometer H, and this varies slightly with the flow. It is possible to consider theoretically the effect of the principal causes which make the heat loss a function of

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* The corrections discussed in this section are all very small, but it has been thought advisable to give a fairly detailed account of them, since an exact estimate of their importance cannot readily be made without a rather close examination of the conditions which govern the heat loss.

the flow. Let C, E, J, S, Q have the significance assigned to them on p. 200. Let $\delta\theta$ be the rise in temperature in a length δx of the calorimeter, θ the excess of the temperature of a point in the calorimeter over that of the jacket, r the resistance of that length of the heating coil which occupies 1 cm. of the axis of the calorimeter, α the temperature coefficient of the material of the heating coil, f the emissivity of the surface of the calorimeter in watts per square centimetre, and p the perimeter of the calorimeter proper. The differential equation which applies after the steady state of temperature has been attained in the calorimeter is

$$\mathrm{JSQ}\,\delta\theta = \mathrm{C}^2 r_0 (1+\alpha\theta)\,\delta x - fp\theta\,\delta x,$$

or

$$\frac{d\theta}{dx} + (fp - \mathrm{C}^2\alpha r_0)\,\theta/\mathrm{JSQ} = \mathrm{C}^2 r_0/\mathrm{JSQ} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

For brevity, write

$$\mathrm{A} = (fp - \mathrm{C}^2\alpha r_0)/\mathrm{JSQ}, \qquad \mathrm{B} = \mathrm{C}^2 r_0/\mathrm{JSQ}, \qquad \gamma = fp/\mathrm{JSQ} \quad . \quad . \quad . \quad (2).$$

Taking the origin of x at the point where the gas first meets the heating coil, the solution of (1), subject to the condition $\theta = 0$ when $x = 0$, is

$$\theta = (1 - e^{-\mathrm{A}x})\,\mathrm{B}/\mathrm{A}.$$

Since A is a quantity of the first order, this equation may be expressed in the form

$$\theta = \mathrm{B}x\,(1 - \tfrac{1}{2}\mathrm{A}x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

the equation applying throughout the length of the heating coil. The temperature θ_l, at the point where the gas leaves the heating coil, is obtained by putting $x = l$ in this equation, l being the length of the axis of the heating coil.

After the gas has passed the heating coil, the differential equation (1) reduces to

$$d\theta/dx + fp\theta/\mathrm{JSQ} = 0.$$

The solution, subject to the condition that the temperature is θ_l at $x = l$, is

$$\theta = \mathrm{B}l\,(1 - \tfrac{1}{2}\mathrm{A}l)\,e^{-\gamma(x-l)},$$

or to the first order

$$\theta = \mathrm{B}l\,(1 - \tfrac{1}{2}\mathrm{A}l)\,\{1 - \gamma\,(x-l)\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

The temperature rise θ_0, measured by the thermometer H, is the mean value of θ over its length, thus

$$\theta_0 = \mathrm{B}l\,(1 - \tfrac{1}{2}\mathrm{A}l)\,\{1 - \gamma\,[\tfrac{1}{2}(m+n) - l]\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

where m and n are the values of x corresponding to the two ends of thermometer H. The true mean temperature over the path, from the beginning of the heating coil to the end of thermometer H, is

$$\theta_m = \frac{1}{n}\left\{\int_0^l \mathrm{B}x\,(1 - \tfrac{1}{2}\mathrm{A}x)\,dx + \int_l^n \mathrm{B}l\,(1 - \tfrac{1}{2}\mathrm{A}l)\,[1 - \gamma\,(x-l)]\,dx\right\}.$$

Using (5)

$$\theta_m/\theta_0 = \frac{1}{2n}\left\{l+\tfrac{1}{6}\mathrm{A}l^2+\gamma l\left[\tfrac{1}{2}(m+n)-l\right]+2(n-l)+(n-l)(m-l)\gamma\right\}.$$

Thus, for a given value of θ_0, the fraction of θ_m which depends upon the flow is given to the first order by

$$\left\{\mathrm{A}l^2+6\gamma l\left[\tfrac{1}{2}(m+n)-l\right]+6(n-l)(m-l)\gamma\right\}/6(2n-l) \quad . \quad . \quad . \quad . \quad (6).$$

Now the heat loss between $x = 0$ and $x = l$ is approximately $\frac{1}{2}lfp\theta$, and that between $x = l$ and $x = n$ is approximately $(n-l)fp\theta$. Hence, if h is the quantity defined on p. 200,

$$h\theta = \left[\tfrac{1}{2}l\theta+(n-l)\theta\right]fp = (n-\tfrac{1}{2}l)\,\theta fp,$$

$$\gamma = fp/\mathrm{JSQ} = h/(n-\tfrac{1}{2}l)\,\mathrm{JSQ},$$

$$\mathrm{A}l = l\gamma-\alpha\mathrm{B}l = hl/(n-\tfrac{1}{2}l)\,\mathrm{JSQ}-\mathrm{C}^2r_0\alpha l/\mathrm{JSQ}.$$

Since $\mathrm{C}^2r_0l = \mathrm{JSQ}\theta$ approximately

$$\mathrm{A}l = hl/(n-\tfrac{1}{2}l)\,\mathrm{JSQ}-\alpha\theta.$$

Substituting in (6) and omitting the term $\alpha\theta$, which does not involve the flow, we obtain for the fraction of the heat loss which involves the flow

$$\epsilon = \{h/\mathrm{JSQ}\}\left\{l^2+6l\left[\tfrac{1}{2}(m+n)-l\right]+6(n-l)(m-l)\right\}/3(2n-l)^2.$$

For the calorimeter employed we may take $l = 4$, $m = 8$, $n = 12$, so that

$$\epsilon = (0\cdot3)\,h/\mathrm{JSQ}.$$

The heat loss in the case of the experiments at steam temperature formed about 8 per cent. of the energy supplied in the large flow, and consequently it may be thought that it is not sufficient to work only to the first order in the above investigation. It must be remembered, however, that all we need in order to correct the results calculated on the assumptions of the equations on pp. 200 and 201 is the percentage variation of the heat loss in the two flows, and since this is only a small fraction of the heat loss itself, it is sufficient to calculate it from the first order terms in the heat loss which involve the flow.

If Q_1 is the quick rate of flow, and Q_2 the slow rate of flow, the heat loss is greater in the slow flow than in the quick flow by $(0\cdot3)\,h^2(\mathrm{Q}_1-\mathrm{Q}_2)/\mathrm{JSQ}_1\mathrm{Q}_2$. It is easy to see that the value of the specific heat calculated from the equations on pp. 200 and 201 must be increased by $(0\cdot3)\,h^2.100/\mathrm{JSQ}_1.\mathrm{JSQ}_2$ per cent. of its value. In order to reduce the value of $\mathrm{CE}/\delta\theta$ (see p. 200) for one experiment of any set to the value which it would have had if the heat loss per degree excess temperature had been the same in that experiment as in the experiment performed with the largest flow, we must decrease it by $(0\cdot3)\,h^2(\mathrm{Q}_1-\mathrm{Q}_2)/\mathrm{JSQ}_1\mathrm{Q}_2$, where Q_2 is the flow for the experiment in question, and Q_1 is the largest flow in the set of experiments. In the case of these experiments on air which were performed at the temperature of the room, the value of h/JSQ_1 was about $\frac{1}{20}$, and the value of h/JSQ_2 about $\frac{1}{10}$, so that according to this correction the specific heat, as calculated from the simple equations on pp. 200, 201, would have to be increased by 1·5 parts per 1000.* For the experiments performed at steam temperature the correction is greater in view of the larger value of h, and amounts to an increase of about 3·2 parts per 1000 on the specific heat.† We meet with another effect at steam temperature, however, which tends to reduce the effect of the above correction. It was observed that the balance point on the platinum thermometer bridge varied with the rate of flow of gas through the apparatus, even when no electric current was passing through the heating coil, the balance point being on the average 1·7 mm. higher for the small than for the large flow, corresponding to an excess rise in temperature between the thermometers of 0°·034 C. in the small flow.

The explanation of this phenomenon is not difficult to understand. The gas on entering the calorimeter proper becomes slightly cooled by the leads of the thermometer K, so that it arrives at K at a temperature slightly below that of the jacket. As it passes through the central portion of the calorimeter, between the thermometers K and H, it becomes heated up again by the jacket, thus there is a slight dip in temperature, as it were, in the neighbourhood of the thermometer K; this dip is greater in the small flow than in the large flow, owing to the greater effect of a given loss of heat on the temperature of the smaller quantity of gas. Thus there is a greater rise in temperature between the thermometers in the small than in the large flow. The effect of this dip in temperature is to cause the mean temperature of the gas between the heating coil and the thermometer H to be below that of the jacket by an amount which is greater in the small than in the large flow. The distance from the centre of the thermometer K to the centre of the heating coil was 5 cm., and the distance from the centre of the heating coil to the centre of the thermometer H was 8 cm., so that the alteration in the rise in temperature between the heating coil and this thermometer in the two flows was $0{\cdot}034 \times 8/13°$ C. approximately. Thus, if we assume that by the time the gas had reached H it had reattained the temperature of the jacket, we see that the excess of the temperature of the jacket over the mean temperature of the gas between the heating coil and H was approximately $\frac{1}{2}(0{\cdot}034)(8/13)$, or 0·01° C. greater in the small than in the large flow. This fact would tend to minimise the heat loss which took place when the gas became heated by the electric current, the effect being greater in the small than in the large

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* This correction is given more accurately on p. 229.

† The corrections thus affect the specific heat to a larger extent than that to which they affect the linear relationship between $CE/\delta\theta$ and the flow. The explanation of this is, that whether we take account of the corrections under consideration or not, a straight line fairly accurately represents the relation between $CE/\delta\theta$ and the flow. The slope of the straight line is, however, different in the two cases.

flow. Since the total rise in temperature in the main experiments was about 5° C., it is easy to see that for the same rise in temperature in the two flows the heat loss was less in the small than in the large flow by 0·4 per cent. of its total value. This effect acts in the opposite direction to that already discussed, and amounts to 6 parts in 10,000 on the specific heat.

In the foregoing discussion it has been assumed that the temperature at every point in a plane perpendicular to the axis of the calorimeter was the same, or, at any rate, that if there was any radial temperature gradient, it was the same in both flows. Now this assumption is justified up to a certain point; the discs of copper gauze referred to on p. 204 would distribute the temperature very uniformly in their immediate neighbourhood; further, the obstructions which the gas encountered in its passage through the calorimeter proper were so numerous that the mixing of the gas must have been very thorough, so that the heat which came from the central portions of the tube to the wall must have been carried mainly by the motion of the gas, and by the conduction of heat through the copper gauze, and not by pure conduction through the gas. This is only another way of stating that the radial temperature gradient in the gas inside the tube was zero. A considerable quantity of heat would be carried through the wall of the tube by the copper gauze, but for the present we will consider what would have been the state of affairs if the heat had been carried entirely by the motion of the gas. This transference of heat to the wall of the tube by the motion of the gas involves a sudden fall in temperature from the gas in the immediate vicinity of the internal wall of the tube to the wall itself, for since from each element of the surface of the tube a definite quantity of heat is being lost per second, and since this heat comes from the gas, each particle of gas must fall in temperature at the moment of striking the tube in order to give out the necessary quantity of heat. The amount by which the gas must fall in temperature will be proportional to the heat loss from the element of tube considered, and inversely proportional to the quantity of gas which strikes that element per second. If the gas is so perfectly mixed that each particle of it strikes the wall of the tube an infinite number of times while it passes through a distance of 1 cm. parallel to the axis of the tube, the fall in temperature of the wall of the tube will be zero at each point; but, obviously, the degree of turbulency of flow which is necessary merely to insure a practically uniform radial distribution of temperature, or, in other words, the degree of turbulency required to insure that practically all the heat which is carried from the central parts of the tube to the wall is carried by the motion of the gas, will fall far short of the infinite degree of turbulency cited above.

In practice we have a degree of turbulency which is sufficiently great to insure that very little heat travels from the central portions of the tube to the wall by pure conduction through the gas, and yet each particle of the gas only strikes the wall of the tube a comparatively small number of times during its passage through a length of tube of 1 cm. for example. It can be shown without very great difficulty that if k

is the average number of times which a particle of gas strikes the wall of the tube in travelling through a distance of 1 cm. parallel to the axis, the effect on the heat loss is to introduce a term which to the first order may be written $-h^2/k\,(n-\frac{1}{2}l)\,\mathrm{JSQ}$ or $-h^2/10k\mathrm{JSQ}$, where n and l have the significance and values accorded to them on p. 212. The correction thus tends in the opposite direction to that discussed on pp. 211–214. Now, in view of the fact that there was only a small space between the wall of the tube and the bundle of glass rods which contained the leads of the heating coil and thermometers, and further, since the heating coil wire and the pieces of wire gauze, &c., offered a large amount of obstruction to the flow of the gas, it is highly probable that k was at least equal to 1. If we take k equal to unity, the correction for the heat-loss term amounts to $-h^2/10\mathrm{JSQ}$, and produces an effect amounting to about 5 parts in 10,000 on the value of the specific heat at 20° C. and 1 part per 1000 on the value of the specific heat at 100° C. The effect tends in the opposite direction to that discussed on pp. 211–214, but the conduction of heat to the walls of the tube by the discs of copper gauze tends to make the value of the correction much smaller than that above deduced, so that it is safe to assume that entire neglect of it does not produce an error of more than 3 or 4 parts in 10,000 on the values of the specific heats.

In the foregoing discussions no account has been taken of the difference in temperature between the external and internal surfaces of the wall of the calorimeter proper. Assuming 0·002 for the thermal conductivity of glass, and taking 0·01 calorie for the average heat loss per second per degree rise in temperature during the experiments, it is easy to calculate from the dimensions of the calorimeter proper that the average difference in temperature between the surfaces of the calorimeter wall for a rise in temperature of 5° C. was about 0°·05 C. Since the heat loss remained constant in the two flows to the first order of its value, the difference in temperature between the surfaces of the wall of the calorimeter proper would remain constant to the first order; in fact, it is easy to see, making use of the investigation given on pp. 211–214, that it would remain constant even in the case of the experiments at steam temperature to about 0°·001 C., so that the effect due to it would eliminate on the two flows certainly to 1 part in 10,000. In the case of the experiments at air temperature the effect would be even less than for steam temperature.

(14) *The Final Experiments.*—The final experiments were divisible into two main sections: the calibration of the fine metal tubes, and the main calorimetric experiments.

(15) *Calibration of the Fine Metal Tubes.*—The method first tried was a modification of that already referred to in connection with the preliminary experiments; several circumstances, which it is unnecessary to enumerate, however, rendered this method somewhat untrustworthy. It was desirable that a method should be employed in which the whole 16 tubes could be calibrated at once; I consequently devised the

following, which is a modification of Regnault's method of measuring the rate of flow, by measuring the fall in pressure in a certain time in a reservoir which supplies the gas. Since the time to be measured was, in the large flow, as small as 90 seconds, it was necessary to devise an automatic method of recording it.

A strong iron vessel of about 50 litres capacity was obtained; it was made thoroughly air-tight, and tested by blowing up a pressure under water. In this way a leak, corresponding to an error of 1 part in 10,000 in the main experiments, could easily have been detected; tests were also made during the main experiments. The mouth of the vessel was closed by a screw cap and washer. From the cap three outlets projected: one, T, for connection to a mercury pressure gauge, one for pumping in the gas, and one for the exit of the gas to the bell of the pressure regulator. The last-named tube was provided with two glass taps, T_1 and T_2 (fig. 6); tap T_3 lead to the bellows. By means of clamps the reservoir was held immersed in a large vessel containing water which was kept stirred. To the steel tape supporting the bell, a metal piece, S, was fixed (fig. 6). When the bell descended, S struck a lever and broke an electrical connection, causing a pen to record a mark on a chronograph. The contact breaker is shown in the figure. c is the lever resting in a **V** groove in the brass support B. W is a weight which keeps the bent end of the lever pressed against the top of the ebonite pillar A, the surfaces of contact being capped with platinum. A piece of platinum wire, P, was soldered to the lever, and caused to dip deeply into a mercury cup in a block of ebonite, M, so that good electrical contact existed between the lever and the mercury cup.

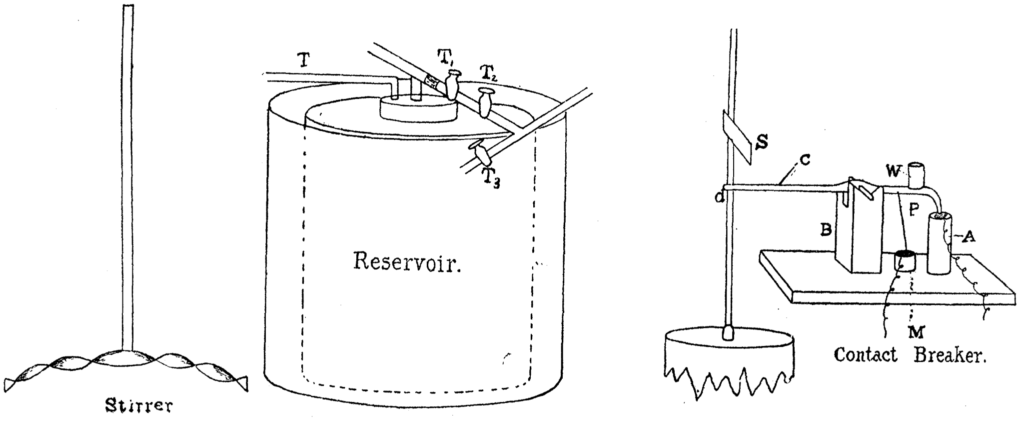

Fig. 6.

The method of performing an experiment was as follows:—The reservoir was first freed from moist air by exhausting it two or three times, and allowing air to enter through the drying apparatus; then, by means of a combined suction and compression pump, air was sucked through the drying apparatus and forced into the reservoir until the excess pressure over that of the atmosphere was about 80 cm. of mercury.

The tap T_1* having been adjusted in a preliminary experiment so that when T_2 was completely opened the gas commenced to pass into the bell at about the required rate, air was pumped from the bellows through T_3 into the bell, T_2 being closed. After the air had passed through the apparatus for some time, and the oil in the oil gauge had settled down, T_3 was turned slightly so as to cause S to hover just a centimetre or so above the end of the lever *c*. T_3 was then completely closed. S immediately started to fall, touched the end of the lever, and at this instant the pen recorded on the chronograph. T_2 was then opened, and air was allowed to flow out of the reservoir and through the apparatus. T_1 was continually adjusted so that the brass piece S did not move too far from the contact breaker *c*. After the pressure in the reservoir had fallen to a value just greater than the minimum required to drive the air through the apparatus at the required rate, T_2 was closed. S then descended, struck the lever, and caused the pen to record on the chronograph.

Now, obviously, between the two instants recorded by the chronograph, an amount of gas passed through the apparatus equal to that which had left the reservoir. It will be seen that it was *not necessary to turn* T_2 *at the instant when* S *touched the lever*; all that was necessary was that the temperature of the gas in the bell should be the same at the start as at the finish,† and it was not necessary that even this should be very accurately true, since the volume of gas in the bell was only a fraction of that of the gas which had passed through the apparatus from the reservoir. By this method everything was rendered entirely automatic, and the times could be obtained as accurately as the chronograph would record them, *i.e.*, to about 0·01 second.

The pressures recorded on the mercury gauge were measured by means of a cathetometer, about half-an-hour being allowed in each case for the gas to take up the temperature of the reservoir. Each reading of the mercury gauge was accompanied by a reading of the temperature of the reservoir; this reading was made with a mercury thermometer which was graduated to 0°·1 C. and read to 0°·01 C., its indications being afterwards compared with a standard. Each reading of the gauge was also preceded by a reading of the barometer. The pressure difference H on the oil gauge was measured immediately after the discharge of the gas from the reservoir, tap T_3 being opened immediately after T_2 had been closed, so as to allow the bellows to pump air into the bell before the latter fell right down. The pump was kept going during the whole of the time that T_3 was closed, an arrangement being made whereby under these circumstances the pump could blow air into the atmosphere. Care was taken to insure that the bell was quite stationary when the pressure difference on the

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* I afterwards found that T_1 was unnecessary. It was quite easy to regulate the gas from the start by means of T_2 alone, and to keep the bell floating in approximately the same position throughout; in fact, I was very much surprised and pleased at the ease with which the flow of gas into the bell could be regulated by means of this tap.

† The precaution was taken of measuring this temperature.

oil gauge was measured, since this pressure difference varied slightly according as the bell was rising or falling, owing to the viscosity of the oil. In some cases the mean of the readings with the bell very slowly rising and very slowly falling was taken. After H had been measured, the taps associated with the oil gauge were turned so as to cause it to record the excess pressure at the high pressure ends of the tubes over that of the atmosphere, in the manner described on p. 208.

It may be thought that since it was impossible to keep the bell quite still during the passage of the gas from the reservoir to the bell an error might arise, owing to the motion of the bell affecting the pressure, and consequently the flow, in virtue of the viscosity of the oil in the pressure regulator. The fact that the bell was in the same position when both times were recorded, however, insured, as will be seen from the following consideration, that no error arose from this cause, even though the motion of the bell might be quite irregular. For let f be the deviation of the rate of flow of the gas from its normal value* owing to the fluctuations in pressure, p the deviation of the pressure of the gas in the bell from its normal value, owing to the motion of the bell. Over the small range of pressure considered we may assume f proportional to p, say $f = cp$. If we assume that the frictional force on the bell was proportional to the velocity for the small velocities under consideration, we have $p \propto dy/dt$, where y is the displacement of the bell from the position in which S touched the lever. Hence $f = c_1\, dy/dt$, c_1 being a constant. If t_1 and t_2 refer to the two times at which the contact was broken, we have for the total error in the flow during the experiment,

$$\int_{t_1}^{t_2} f\,dt = \int_{t_1}^{t_2} c_1 \frac{dy}{dt}\,dt = \int_0^0 c_1\,dy = 0,$$

since initial and final positions of the bell were the same. Hence the compensation is exact.

The volume of the reservoir was determined by filling it with successive weighed quantities of water. The weights were corrected to *vacuo*, and corrections were made for the temperature of the water. The effect of pressure in altering the volume of the reservoir was investigated by filling it and its connections with water, forcing more water in until the pressure rose by about 80 cm. of mercury, and then noting the pressures as successive quantities of water were allowed to escape through a side tube. The corrections, as determined in this way, contain the corrections for the alteration in volume due to the mercury in the gauge tube altering its position as the pressure changes. The observations, full details of which are preserved in the archives, lead to the expression $V = 51094 + 5{\cdot}355P + k$ for the volume of the reservoir as a function of the internal excess pressure P. The expression $(5{\cdot}355P + k)$ represents the alteration in volume due to internal pressure. The smoothed values of k for different values

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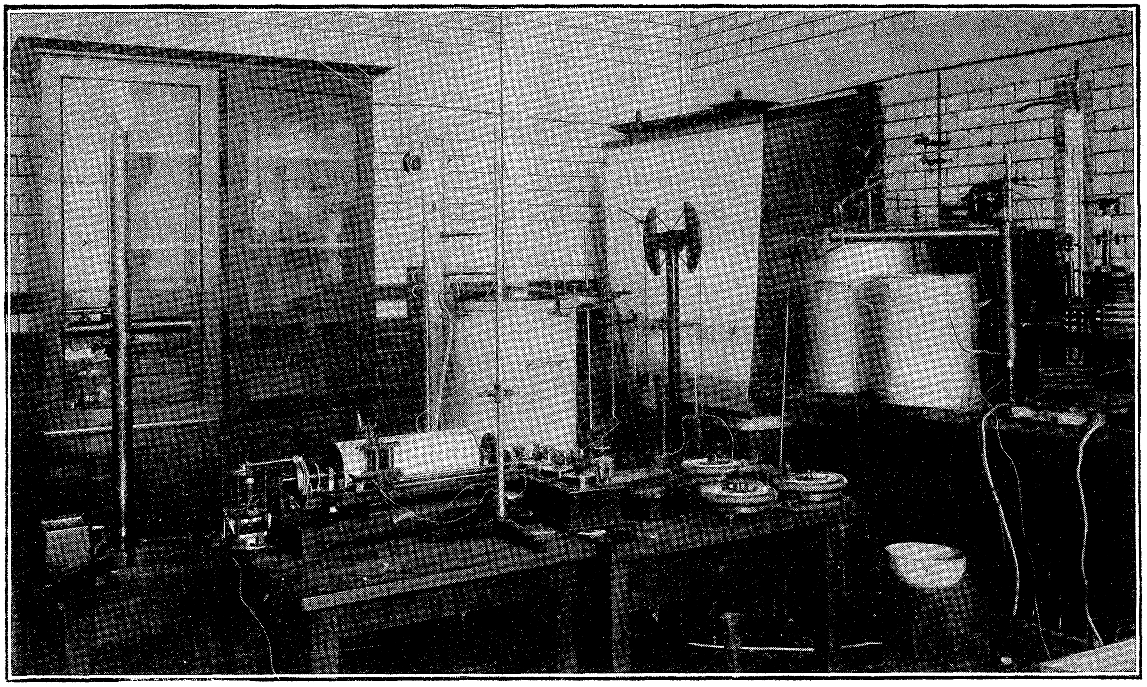
* By the normal value is meant the value when the bell is still.



of P are given in the adjoining table. The accompanying illustration shows the main portions of the apparatus used in the calibration of the fine tubes, together with several other portions of apparatus used in the calorimetric experiments. The cathetometer is shown to the left of the picture; next to it is the chronograph. To the right of this and behind it are seen the mercury gauge, gas reservoir, and pressure regulator, with the contact breaker in the back ground. To the right of the pressure regulator is the tank containing the tubes, and to the right of this the calorimeter and oil gauge. The arrangement for siphoning water round the jacket of the calorimeter during the calibration may also be seen in the illustration.

P, cm. Hg . .	0	10	20	30	40	50	60	70	80
k, c.cm. . . .	– 1	12	24	31	32	27	18	8	– 3

(16) *Calculation of the Results.*—If the gas strictly obeyed the simple gas law over the range of pressure to which it was subjected in the reservoir, the mass Q of gas which flowed through the tubes in any experiment would be simply $(P_1V_1/\theta_1 - P_2V_2/\theta_2)/R$, where the suffixes relate to the measurements taken before and after the flow of gas respectively, and R is the gas constant for 1 gr. of gas. Since, however, the gas does not obey the simple law, a correction must be applied. REGNAULT has shown that for air, if $p_1 = 74$ cm. and $p_2 = 148$ cm. (which represents the range of pressure employed in the present experiments), then at constant

temperature $p_1V_1/p_2V_2 = 1·00141$ approximately. Hence to correct the values of PV/θ to the values they would have had if the gas had obeyed Boyle's law, taking our standard pressure as that due to 76 cm. of mercury, we find that the observed values of PV/θ must be multiplied by $1+(0·00141)(P-76)/74$. A further small correction is necessary on account of the departure of the gas from the linear relationship between PV and θ over the range of temperature from 0° C. up to the temperature of the reservoir, but this may be conveniently applied to the final value of the specific heat. A lengthy series of preliminary observations, full details of which are preserved in the archives, was performed with a set of ten tubes, and practice and experience with the method gained. The agreement in these experiments was very satisfactory. The following table is an abridged record of the calibration of the sixteen tubes used in the final experiments, the value 0·0012928 gr./c.c. being taken for the density of air at N.T.P. in the calculation of the gas constant R. The experiments were made to determine how the flow varied with the pressure difference between the ends of the fine tubes (H), the mean pressure in them (*P*), and their temperature (*t*) :—

(17) Abridged Table for the Calibration of the Tubes for Air.

Experiment .	1, 2, 3.	4, 5, 6, 7.	8.	9, 10.	11, 12.	13, 14.	15, 16.	17, 18.	19, 20.
Q, gr./sec.	0·66729 0·66697 0·66762	0·30285 0·30328 0·30327 0·30325	0·29193	0·38534 0·38529	0·51825 0·51829	0·66214 0·66228	0·29730 0·29716	0·65549 0·65493	0·29746 0·29783
Q (mean values)	0·66729	0·30316	0·29193	0·38532	0·51827	0·66221	0·22723	0·65521	0·29764
P, cm. Hg	78·15	78·61	78·745	79·26	78·47	76·78	77·00	78·82	78·69
H, cm. oil	29·24	10·56	10·057	14·16	20·90	29·45	10·50	29·00	10·59
t, temp. tubes	18° C.	18° C.	18° C.	18° C.	18° C.	18° C.	18° C.	22°·8 C.	22°·8 C.

Of course the values of H, *P* and *t* were not quite the same in each of the individual experiments from any set in the above table, it was easy, however, by first obtaining a preliminary empirical equation, to reduce the values of Q for any set to the same values of H, *P* and *t*. The above values of H, *P* and *t* corresponding to the temperature 18° C. are satisfied to 1 part in 10,000 by the equation

$$Q = 0·0046489\{1-0·0095[P-78]\}\{\sqrt{(491·29+271·19H-2·91H^2)}+3·0262H-22·17\},$$

and it is satisfactory to observe that this order of accuracy is approached even in the case of Experiment 8, and the mean of Experiments 15 and 16, and these experiments took no part in the determination of the constants of the equation. The full account of the method by which the equation was deduced is contained in the archives.

The percentage decrease in Q per degree increase in t varies with H; it can be shown from the above table, combined with the empirical equation, to amount to 0·385 per cent. for $H = 29$ cm. and 0·444 per cent. for $H = 10·59$ cm. To obtain the percentage decrease for intermediate values of H, it is sufficiently accurate to assume a linear variation with the flow. It is interesting to observe that the linear relation gives 0·5 for the percentage decrease when the flow is zero, and this is not far from the theoretical value calculated by neglecting the inertia effects, which value we should of course expect to obtain for indefinitely small values of the flow.

(18) *The Main Calorimetric Experiments.*—In the experiments at air temperature water was siphoned from the tank N, fig. 2, round the double walls of the calorimeter jacket into another vessel, from which it was poured back again into the tank, where it was kept well stirred. The apparatus was tested for leaks, and the pump was started. The temperature of the gas was noted by means of the thermometer K when it had become steady, *i.e.*, after about half-an-hour. The thermometers were then arranged differentially, and the balance point on the bridge was again determined. The electric current was then started through the heating coil, and the rheostat was adjusted so that the rise in temperature was about 5° C. or 6° C.; the current remained almost perfectly steady when the various resistances in the circuit had warmed up to their final values. The screw stirrer in the tank containing the tubes was started, and in about 20 minutes the balance point on the bridge became steady to about 0·2 mm., *i.e.*, to about 0°·005 C.; but the final readings were not taken until about half-an-hour after the commencement of the heating, by which time the balance had usually become steady to 0·1 mm. or less. The clip A, fig. 2, was adjusted so that the bell of the pressure regulator was quite still, or moving so slowly that it took about 10 minutes to rise or fall two or three centimetres in order to avoid fluctuations in pressure. This adjustment could be performed with comparative ease after a little practice. The bridge reading, potentiometer readings across the secondary standard and across the heating coil, and the gauge reading were then observed over a period of three or four minutes in order to make sure that no fluctuations were taking place, or that, if there were any very slight fluctuations, they were consistent with one another. The temperatures of the gauge, tubes, manganin coil, and cadmium cells were then noted, and the potential and current leads were quickly interchanged (see p. 204). While the temperature conditions were becoming constant, the potentiometer reading across the cadmium cells was taken, also the reading of the barometer and its temperature. When the temperature rise had again become steady, the bridge gauge and potentiometer readings

were taken as before, as were also the various temperature readings. The taps T_1 and T_2 (fig. 2) were then turned so as to cause the gauge to measure the excess pressure at the high pressure ends of the tubes over that of the atmosphere. While the oil was settling down in the gauge, the potentiometer reading across the cadmium cells was again taken, and the barometer was read. The gauge reading having been taken, the electric current was stopped, and the gas was allowed to flow through the calorimeter to cool it down. At the end of about half-an-hour the balance on the bridge became steady, and usually agreed with that obtained at the beginning of the experiment to less than 0·1 mm. The balance point having been obtained, the bridge connections were again altered, and the actual temperature of the gas was measured with the thermometer K. The current of gas was then stopped, the throttles for altering the flow were changed, and tested for leaks, and another run was taken in a similar manner, the electric current being adjusted so that the rise in temperature was almost the same as before.

The experiments at steam temperature were performed in a similar manner, except that the current of water round the calorimeter jacket was replaced by a current of steam, which was allowed to flow for about an hour before the experiment was started. In some of the experiments at steam temperature the steam was supplied from two cans of water arranged in parallel; when one can showed signs of giving out the other was started. It was found that under these conditions the temperature readings did not remain absolutely constant, for the pressure of the steam varied with the amount of water in the cans. I consequently fastened a horizontal tube into the side of a can, bent the end up vertically, and fixed it under a tap which was allowed to drip upon it at a rate slightly greater than the rate of ebullition of the water in the can. Thus the level of the water in the can was kept constant, the excess of water running over the edge of the tube. The vertical portion of the tube was of fairly small bore, so that if the rate of ebullition altered momentarily, as it sometimes did, the sudden fall of water in the tube due to the fall in pressure did not cause any appreciable quantity of cold water to suddenly rush into the can.

(19) *The Heating Effect of the Current Leads.*—A main run having been taken in the manner above described, and the balance point on the bridge having been redetermined with no electric current flowing, the external connections to the current and potential leads were changed so that the current could flow through the leads Pp (fig. 4). The electric current was adjusted to practically the same value as in the main run, and the rise in temperature of the gas was measured. The connections were then altered so that the current flowed through the leads Qq, and the temperature was again measured. A large number of experiments were performed, details of which are preserved in the archives. The following table gives the mean values of $(\delta t/t)\,100$ for the large and small flows at steam and air temperatures; δt represents the rise in temperature due to the leads under consideration, corresponding to the rise in temperature t for the same current in the main experiment. The difference

between the values for the arrangement Qq and Pp is due to the fact that the platinum loops (see p. 203) associated with Qq and Pp were not exactly equal in resistance.

TABLES of Mean Values of $(\delta t/t)\,100$.

Air Temperature.

	Quick flow.	Slow flow.
Qq	2·064	2·161
Pp	1·716	1·843
Pp+Qq	3·780	4·00

Steam Temperature.

	Quick flow.	Slow flow.
Qq	2·017	2·062
Pp	1·711	1·72
Pp+Qq	3·73	3·79

The correction is thus a small one, only amounting to about 2 per cent. of the total heating effect. It will be observed that the heating effect of the leads was slightly greater for the slow than for the quick flow at air temperature, which is what we should expect if, in those experiments, there was a term proportional to the square of the electric current, which represented heat conduction along the leads. The variation of the above numbers under different conditions is only what might be expected in view of the complicated conditions governing the heat loss in the leads, which would vary with the temperature of the calorimeter and the rate of flow of the gas through it. It is only by a method such as the above, in which the corrections are determined under the conditions which hold in the main experiments, that such small variations as are shown in the above tables could be detected and successfully measured.

(20) *Calculation of the Results.*—In the main runs the current passed either through the leads Qp or Pq. If the ratio of the rise in temperature due to the leads to the total rise in temperature be denoted by a for the first arrangement, and b for the second, the values of $(a+b)$ for different conditions are equal to the one-hundredth parts of the corresponding quantities in the third line of the above table. Now, in taking into account the heating effect of the leads, the simple equations on pp. 200 and 201 must be modified by replacing $\delta\theta$ by $\delta\theta\,(1-a)$, and $\delta\theta\,(1-b)$ in the case of the arrangements Qp and Pq respectively. In those experiments where the run with

arrangement Qp was immediately followed by another with arrangement Pq, in which the flow of gas and rise in temperature were almost identically the same (see p. 222), we have

$$C_1E_1/\delta\theta_1\,(1-a) = JSQ_1+h \text{ for the arrangement } Qp,$$

and

$$C'_1E'_1/\delta\theta'_1\,(1-b) = JSQ'_1+h \text{ for the arrangement } Pq.$$

Hence, since a is nearly equal to b, and $C_1E_1/\delta\theta_1$ is nearly equal to $C'_1E'_1/\delta\theta'_1$, we have, to the second order of approximation

$$[C_1E_1/\delta\theta_1+C'_1E'_1/\delta\theta'_1]\,[1+\tfrac{1}{2}(a+b)+a^2] = JS\,(Q_1+Q'_1)+2h.$$

A similar equation represented the combination of the two experiments for some other value of the flow, the proper value of $(a+b)$ being substituted, and from this equation and the above equation, h could be eliminated, and JS determined in terms of measured quantities. This was the usual method of applying the correction for the leads. In certain cases, notably in the case of the experiments on carbon dioxide, the runs were only taken with the electric current passing through the leads Qp, but the correction in these cases could easily be calculated and applied.*

The temperature of the gas was not always exactly the same in the slow and quick flows, and it was necessary to consider whether such small differences as occurred were of appreciable importance. If the temperature varies, the specific heat varies, and also the value of the quantity h. It is easy to see that with such small variations as occurred, the first correction was entirely negligible in the case of air. With regard to the second, it can be easily shown that if the heat loss were entirely due to radiation, h would, on the assumption of STEFAN'S law, vary approximately as the cube of the absolute temperature. The actual measurements of h in the neighbourhood of 20° C. and 100° C. are more accurately represented by $h = 1{\cdot}44\theta^{2{\cdot}16}\times10^{-7}$, showing h to be proportional to a lower power of the absolute temperature than the cube, which is what we should expect since part of the heat loss was due to conduction and convection. The above expression enables the corrections for the variation of h in the two flows to be calculated; they are all small, only amounting to one or two parts in 10,000 on the specific heat.

The complete tables for the calorimetric experiments are preserved in the archives, but the tables which follow, and which are considerably abridged, show the main quantities upon which the values of the specific heats depend.

The second column gives the rate of flow of the gas in grammes per second. The third gives the rise in temperature $\delta\theta$ corrected to the absolute scale by multiplying the rise $\delta\theta_{pt}$ as measured on the platinum scale by $\delta\theta/\delta\theta_{pt}$, this quantity being obtained by differentiating the difference formula $\theta-\theta_{pt} = d.\theta\,(\theta-100)/10^4$. The fourth column gives the values of $CE/(1-a)$ or $CE/(1-b)$ according as the run in question was performed with the arrangement of leads Qp or Pq. These quantities represent the

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* The method of calculating a and b is described in the records preserved in the archives.

watts supplied, corrected for the heating effect of the leads. As is shown above, it is only necessary in the calculations to know the values of

$$[C_1E_1/\delta\theta_1 + C'_1E'_1/\delta\theta'_1]\,[1+\tfrac{1}{2}(a+b)+a^2],$$

where the symbols have the significance already accorded to them, but, for the sake of clearness, the corrected values of CE are recorded for each run in the table.

The fourth column gives the mean temperature of the gas over the range of temperature through which it was heated. The sixth column gives the values of h in watts per degree. The seventh and eighth columns give the values of the specific heat, the numbers in the latter column being reduced to a standard temperature, and the last column gives the deviation of the specific heat from the mean value, the error being reckoned as a percentage on the specific heat. In addition to the runs taken for the determination of the specific heats, runs with intermediate rates of flow were taken for the purpose of testing the linear relationship between CE/$\delta\theta$ and the flow. For the sake of clearness, however, the data for these runs are omitted from the following tables, and are collected together in tables by themselves on p. 229.

The pressure at which the specific heat was determined, may be taken as that due to 76 cm. of mercury, since there was practically no difference between the pressure in that portion of the calorimeter where the rise in temperature took place and the atmosphere. The value of $\partial S/\partial P$ may be calculated, and it can easily be shown that a change of 1 cm. in the barometric height cannot produce a change in S of more than about 1 part in 40,000, so that it is unnecessary to take into consideration the fluctuations of the atmospheric pressure during the experiments.

(21) ABRIDGED Table for the Main Calorimetric Experiments on Air.

Table I.—Air Temperature.

Date.	Flow, Q.	Rise, $\delta\theta$.	Watts, CE.	Mean temperature.	h.	Specific heat.	Specific heat at 20° C.	e.
								per cent.
August 12 .	0·29526	5·1438	1·6855	20·5	0·02975 at 20°·7 C.	0·24142 at 20°·7 C.	0·24141	+0·02
	0·29463	5·1526	1·6850					
	0·67044	5·1362	3·6277	20·7				
	0·67041	5·1356	3·6272					
August 13 .	0·67306	5·0884	3·6073	20·3	0·03136 at 20°·3 C.	0·24084 at 20°·3 C.	0·24084	−0·22
	0·67294	5·0884	3·6069					
	0·30216	5·0796	1·7046	20·5				
	0·30191	5·0823	1·7045					

Mean value for the specific heat at 20° C. = 0·24137 cal. per gr. degree.

Table I.—Air Temperature (continued).

Date.	Flow, Q.	Rise, $\delta\theta$.	Watts, CE.	Mean temperature.	*h*.	Specific heat.	Specific heat at 20° C.	*e*.
								per cent.
August 14 .	0·66907	5·0980	3·6022	20·8	0·02993 at 20°·8 C.	0·24189 at 20°·8 C.	0·24188	+0·21
	0·66923	5·0962	3·6003					
	0·30234	5·0612	1·6991	21·0				
	0·30240	5·0577	1·6980					
August 14 .	0·30197	5·0698	1·7000	21·2	0·03035 at 21°·3 C.	0·24165 at 21°·3 C.	0·24164	+0·11
	0·30187	5·0684	1·6994					
	0·66725	5·0842	3·5816	21·3				
	0·66738	5·0813	3·5790					
August 25 .	0·30286	5·4232	1·8267	20·0	0·03116 at 20°·0 C.	0·24151 at 20°·0 C.	0·24151	+0·06
	0·30306	5·4137	1·8254					
	0·66390	5·4386	3·8158	20·0				
	0·66381	5·4386	3·8127					
August 27 .	0·65683	5·4939	3·8097	19·3	0·03180 at 19°·3 C.	0·24100 at 19°·3 C.	0·24101	−0·15
	0·65646	5·4912	3·8064					
	0·30366	5·4631	1·8440	19·6				
	0·30305	5·4603	1·8423					
August 28 .	0·30210	5·4846	1·8440	19·7	0·03189 at 20°·0 C.	0·24104 at 20°·0 C.	0·24104	−0·14
	0·63689	5·4826	3·6929	20·0				
August 28 .	0·66492	5·2510	3·6870	19·3	0·03049 at 19°·3 C.	0·24166 at 19°·3 C.	0·24167	+0·12
	0·30412	5·2330	1·7674	19·5				

Mean value for the specific heat at 20° C. = 0·24137 cal. per gr. degree.

ABRIDGED Table for the Main Calorimetric Experiments on Air.
Table II.—Steam Temperature.

Date.	Flow, Q.	Rise, $\delta\theta$.	Watts, CE.	Mean temperature.	*h*.	Specific heat.	Specific heat at 100° C.	*e*.
								per cent.
August 15 .	0·65484	5·5036	3·9349	101·5	0·05206 at 101°·5 C.	0·24219 at 101°·5 C.	0·24217	−0·06
	0·65474	5·5013	3·9332					
	0·29481	5·4800	1·9187	100·8				
	0·29444	5·4773	1·9178					
August 16 .	0·65906	5·4783	3·9404	101·7	0·05291 at 101°·7 C.	0·24185 at 101°·7 C.	0·24183	−0·20
	0·65874	5·4750	3·9355					
	0·29864	5·4592	1·9355	100·9				
	0·29858	5·4609	1·9362					
August 21 .	0·66488	5·4594	3·9653	102·1	0·05236 at 102°·1 C.	0·24252 at 102°·1 C.	0·24250	+0·08
	0·66488	5·4537	3·9619					
	0·30089	5·4358	1·9422	101·4				
	0·30030	5·4385	1·9387					
August 23 .	0·29976	5·5165	1·9648	101·3	0·05200 at 102°·0 C.	0·24273 at 102°·0 C.	0·24271	+0·16
	0·29954	5·5272	1·9649					
	0·65804	5·5441	3·9899	102·0				
	0·65813	5·5371	3·9855					
August 24 .	0·65326	5·7994	4·1434	101·9	0·05269 at 101°·9 C.	0·24238 at 101·9° C.	0·24236	+0·02
	0·65284	5·7945	4·1388					
	0·29823	5·7558	2·0422	101·2				
	0·29850	5·7509	2·0403					

Mean value for the specific heat at 100° C. = 0·24231 cal. per gr. degree.

The following two tables are records of the results for runs taken with flows intermediate between the largest and smallest flows for the purpose of testing the linear relationship between Q and CE/$\delta\theta$. The second, third, and fourth columns give the values of Q for the largest, smallest, and intermediate flows respectively. The fifth column gives the observed values of $CE/\delta\theta$ for the intermediate flows, reduced to the values they would have had if the experiments which they represent had been performed at exactly the same temperature as those to which the corresponding largest and smallest flows are referred. The sixth column gives the values of $CE/\delta\theta$ calculated by using the values of S and h obtained for the corresponding largest and smallest flows. The last column gives the percentage difference between the observed and calculated values of $CE/\delta\theta$ the percentage being reckoned in the largest value of $CE/\delta\theta$ in the particular set of observations in question :—

AIR Temperature.

Date.	Q largest.	Q smallest.	Q intermediate.	$CE/\delta\theta$ observed.	$CE/\delta\theta$ calculated.	Error on largest flow.
						per cent.
August 13 . .	0·6730	0·3021	0·38599	0·42051	0·41995	−0·08
	0·6730	0·3021	0·54963	0·58503	0·58468	−0·05
,, 27 . .	0·6568	0·3036	0·54373	0·57904	0·57955	+0·07

STEAM Temperature.

Date.	Q largest.	Q smallest.	Q intermediate.	$CE/\delta\theta$ observed.	$CE/\delta\theta$ calculated.	Error on largest flow.
						per cent.
August 15 . .	0·6548	0·2948	0·43620	0·49334	0·49365	+0·04
,, 21 . .	0·6649	0·3009	0·65832	0·71926	0·71972	+0·06
,, 23 . .	0·6580	0·2997	0·53011	0·59000	0·58985	−0·02
,, 24 . .	0·6532	0·2985	0·50528	0·56430	0·56460	+0·04

To the above mean values of the specific heats a few corrections remain to be applied—

(1) The corrections discussed on pp. 211–215. The values of the corresponding rates of flow were practically the same for all the final experiments from which the specific heats were calculated, so that the correction is one which may conveniently be applied to the mean value of the specific heat. Taking the mean value of $(0·3)\, h^2/JSQ_1 . JSQ_2$ for all the experiments at 20° C., we find that the correction to be applied to the specific heat at this temperature is additive and amounts to 1·3 parts per 1000. For the experiments at 100° C. the corresponding correction amounts to 3·3 parts per 1000. In the latter case, however, we have the correction mentioned on p. 214 (lines 7 *et seq.*), which is subtractive and amounts to 6 parts in 10,000, so that the two corrections together amount to 2·7 parts per 1000.

(2) A correction for the fact that, in the calibration of the tubes, a linear relation between PV and θ was assumed to hold over the range of temperature 0° C. to 17° C.

(p. 221). Taking the pressure coefficient over this range to be 0·003674, the correction can be shown to be additive and to amount to 1·9 parts in 10,000.

(3) A correction to represent the deviation of the ice-point and fundamental interval of the mercury thermometer to which the temperatures of the reservoir were referred from their proper values. The reading of the thermometer at 0° C. was 0·00° C., and the correction to be applied to the fundamental interval was −0·03° C. The correction to be applied at 17° C. is consequently quite negligible.

(4) A correction for the reduction of the readings of the above mercury thermometer to the absolute scale. The correction is subtractive, and amounts to 2·2 parts in 10,000 on the specific heat.

(5) A correction for the fact that the volume of the reservoir was altered by the external pressure of the water in the bath which surrounded it. The corrections for internal pressure were taken into account when working out the results for the calibration of the tubes, but the above correction was left to be applied to the calculated value of the specific heat. It is dealt with fully in the records preserved in the archives, and is shown to be additive and to amount to 2 parts in 10,000.

Hence the several corrections amount to total additive corrections of 1·5 parts per 1000 on the value of the specific heat at 20° C., and 2·9 parts per 1000 on the value at 100° C. The corrected values of the specific heat are

$$\mathbf{S = 0{\cdot}24173}\ \text{cal. per gr. degree at } \mathbf{20}^\circ\ \text{C.,}\quad \mathbf{S = 0{\cdot}24301}\ \text{cal. per gr. degree at } \mathbf{100}^\circ\ \text{C.,}$$

the results being expressed in terms of the calorie at 20° C.

(22) *Comparison of the Results with Theory.*—Prof. CALLENDAR has shown* that the characteristic equation of a gas may be simply and accurately expressed in the form $v-b = \mathrm{R}\theta/p-c$, where b is a constant, R is the gas constant, and c is a function of the temperature of the form $c = c_0\,(\theta_0/\theta)^n$. The behaviour of air is well represented if we take $c_0 = 1{\cdot}48$ and $n = 1{\cdot}5$. It is convenient to measure p with a unit of pressure of 10^6 dynes (75 cm. Hg), in which case if S represents the value of the specific heat at a pressure p and a temperature θ, and S_0 the value at zero pressure and at the same temperature

$$\mathrm{S} = \mathrm{S}_0+n\,(n+1)\,cp/\theta,$$

where S and S_0 are both measured in terms of a unit of heat of 10^6 ergs or 1/41·80 calorie, the calorie referred to being the calorie at 20° C., which is taken equal to $4{\cdot}180\times10^7$ ergs. Substituting the value of c at 50° C. we find $\mathrm{S}-\mathrm{S}_0 = 0{\cdot}00032$ calorie. Assuming a linear variation of the specific heat with temperature over the small range of variation of 0·5 per cent. between 20° C. and 100° C., my own observations give 0·24221 cal. per gr. degree for the value of S at 50° C. Hence $\mathrm{S}_0 = 0{\cdot}24189$ at 50° C. It can be shown that if s_0 is the specific heat at constant

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* 'Phil. Mag.,' S. 6, vol. 5, p. 91 (1903).

volume and at zero pressure, and if S_0 and s_0 refer to the same temperature, $S_0 - s_0 = R = 2 \cdot 8727 \times 10^6$ C.G.S. units, or 0·06872 calorie. JOLY has measured the specific heat of air at constant volume by the steam calorimeter.* In his calculations, however, he assumes REGNAULT'S value for the latent heat of steam (L = 536·7 cal./gr.). This value is almost certainly too low. HENNING has recently measured the latent heat of steam† and found 538·9 cal./gr., while JOLY'S own observations with the steam calorimeter lead to the value 540·2 in terms of the calorie at 20° C. Assuming this value to correct JOLY'S results for s, and extrapolating to zero pressure, we obtain for the value of s_0 at 50° C. (the temperature at which JOLY measured it) $s_0 = 0 \cdot 1732$. This value of s_0, in conjunction with my own value of S_0 at 50° C., gives 0·0687 calorie for $S_0 - s_0$, which agrees with the above value of R to less than $\frac{1}{1000}$ of the specific heat.

(23) *Criticism of Previous Results.*—All previous determinations of the specific heat of air at constant pressure have given a lower value than 0·2422 (my own value at 50° C.). REGNAULT obtained 0·2375, which is lower than 0·2422 by about 2 per cent. One has only to read REGNAULT'S paper to feel convinced that an error of 2 per cent. could not have arisen in his experiments from lack of care in the observations. If my own value is correct, it is to some point in the theory of REGNAULT'S method that we must look if we are to explain an error of 2 per cent.

Now, in order to determine the alteration $\Delta\theta$ in the temperature of the calorimeter per minute due to radiation, conduction, &c., REGNAULT assumed an equation of the form $\Delta\theta = A - B\theta$, where θ is the excess of the temperature of the calorimeter over that of the room, $B\theta$ represents the radiation loss per minute from the calorimeter, and A represents the alteration in the temperature of the calorimeter per minute due to conduction of heat from the heating bath to the calorimeter along the pipe connecting them. The total alteration in temperature, due to the above causes during the experiment, was obtained by summation. The constants A and B were determined from two equations obtained by observing the alteration in temperature of the calorimeter before and after the main experiment. Now, since there was no gas flowing through the connecting pipe when the observations which determined the constants A and B were made, the conduction effect must have been very different from what it was when gas was flowing through the pipe.

To fix our ideas, suppose the temperature gradient in a connecting pipe is uniform when no gas is flowing through it. Now, when the hot gas passes through the tube, it will keep the temperature of the latter up, so that the temperature gradient in the tube *near the heater* will be very much reduced; in fact, it is possible that it may be reduced practically to zero, so that no heat will be conducted from the heater to a point in the pipe a little distance from it. Heat will certainly be conducted to the calorimeter through the pipe, but this heat will come from the gas itself and not

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* 'Phil. Trans.,' 1904.

† 'Annalen der Physik,' No. 10, 1904.

directly from the heater. Thus we should expect that the term A, which REGNAULT found to represent 5 per cent. of the total rise in temperature of the calorimeter per minute, might be practically zero when the gas was flowing through the pipe. Further, the passage of the gas would increase the radiation loss from the pipe, since it would increase its mean temperature. Both of these effects tend in the same direction, but the second is probably small. The form of connecting pipe used by REGNAULT would tend to minimise the above effects, but it is impossible to say by how much.

It is probable that the true value of A lies somewhere between zero and the value found by REGNAULT. If we take A equal to zero, REGNAULT'S experiments give 0·248 for the specific heat. If we take for A the mean between the two extreme values, zero and REGNAULT'S value, the specific heat works out to 0·242, which is in close agreement with my own value, 0·2422. The above criticism applies not only to the work of REGNAULT, but also to most of the more recent measurements of the specific heats of gases at constant pressure, and it is possibly owing to this fact that these measurements give values for the specific heats which are so much lower than my own values and the theoretical values.

(24) *The Specific Heat of Carbon Dioxide.*—The carbon dioxide was supplied by the manufacturers in iron bottles, each bottle containing about 20 lb. of liquid CO_2. A preliminary test showed that the gas contained about 0·5 to 0·7 per cent. of air and about 0·5 to 0·7 per cent. of water vapour. It was consequently necessary to pass it through the drying apparatus used in the experiments on air, the KOH tower was, however, replaced by a tower containing crystals of calc. spar, which served to collect any acid fumes from the sulphuric acid rocker, without introducing any gas other than carbon dioxide. The iron bottles when supplying the gas were fitted with an automatic pressure reducer, which prevented the pressure in any part of the apparatus attaining a dangerously high value. The T-piece A (fig. 2) was replaced by a large glass tap, followed by a piece of rubber tubing which could be partially constricted by a clip, thus all possibility of air diffusing back into the carbon dioxide was prevented. The flow of gas into the pressure regulator could be roughly adjusted by means of the tap, and more finely by means of the clip. It was impossible to get rid of all the air in the CO_2, but I found that, after a large quantity of gas had been taken from a bottle, the remaining gas was practically pure, the percentage of air falling from about 0·6 per cent. in the case of a full bottle to about 0·01 per cent. in the case of a bottle which was nearly empty. Unfortunately I had used a large quantity of the gas before I discovered this fact, but I was able, however, to calibrate the fine tubes with pure CO_2 taken from bottles which were nearly empty, and in the later calorimetric experiments I adopted the following device. Two bottles, A and B, were arranged so as to be able to supply gas in parallel. The automatic pressure reducer was fixed to the tube joining the bottles. A was half empty and B was full. Gas was passed through the apparatus from B until the temperature conditions were

nearly steady. A was then opened and B shut off, so that the final readings were taken with the pure gas from A passing through the apparatus. The process could be repeated until A was empty, by which time B was half empty. A was then replaced by a full bottle, and B was used for supplying the gas while the measurements were being taken, and so on.

This method enables one to make use of all the gas from the bottles, and yet to use only pure CO_2 when taking the actual measurements. As a matter of fact, the presence of a small quantity of air in the CO_2 only produces a very small effect on the measured value of the specific heat. The volumes of air and CO_2 which flow through the fine tubes for a given pressure difference between their ends are practically the same as may be seen from the calibration tables; further, the thermal capacities of equal volumes of air and CO_2 are in the ratio 1 to 0·77. Hence, if as much as 1 per cent. of CO_2 were replaced by an equal volume of air, which would leave the apparent value of Q unchanged, the thermal capacity would only be reduced by 0·23 per cent. It is probable that in no case was there more than 0·4 per cent. of air in the CO_2 when the measurements were taken, as the bottles had always been running for some time before the temperature conditions had become steady, so that the effect of the presence of air in the CO_2 never probably amounted to more than one or two parts per thousand on the energy supplied in any experiment.

Before commencing the experiments it was necessary to get rid of all the air in the different parts of the apparatus; this was done by exhausting the air from the different parts and allowing CO_2 to take its place, the operation being repeated several times.

(25) *The Calibration of the Fine Tubes.*—The method adopted was similar to that described for air. For filling the reservoir with CO_2 a combined suction and compression pump was used, the gas being drawn through the sulphuric acid rocker and forced into the reservoir. In order to minimise the time taken for the oil in the oil gauge to settle down in an experiment, it was previously blown up to a reading a little above that at which it was finally expected to settle in the experiment, and the glass taps were turned so as to keep it there while the oil on the sides of the gauge settled down. After about twenty minutes the current of gas was started, and the actual experiment was commenced, the taps being turned so that the gauge was under the influence of the pressure difference set up by the gas flowing through the fine tubes.

The following abridged table represents the results for the calibration and corresponds to the table given on p. 221 for air. The complete records of the calibration are preserved in the archives. The correction of the value of PV to the value of P_0V_0, which it would have had if the gas had obeyed BOYLE's law, was obtained as in the case of air by an expression of the type $P_0V_0 = PV\{(P-76)m+1\}$, where m is a quantity which may be determined from REGNAULT's tables. In the case of CO_2 there was an appreciable difference between the values of m for the high and low pressures in the reservoir; the value for each case was, however, easily deduced from REGNAULT'S observations. The expression for Q in terms of H and P was found to be

$$Q = 0{\cdot}0071081\{1+0{\cdot}0089\,(P-78)\}\,\{\sqrt{(0{\cdot}181+70{\cdot}39H-2{\cdot}136H^2)}+4{\cdot}2869H-0{\cdot}425\},$$

the equation applying when the temperature of the tubes was 16°·7 C.

(26) ABRIDGED Table for the Calibration of the Fine Tubes for CO_2.

Experiment . .	1, 2, 5, 13.	8, 9.	3, 4.	7.	6.	10.	11, 12.
Q, gr./sec.	0·94967 0·94831 0·94760 0·94750	0·42844 0·42764	0·83384 0·83422	0·91553	0·93493	0·41426	0·94026 0·93913
Q (mean values)	0·94827	0·42804	0·83403	0·91553	0·93493	0·41426	0·93969
P, cm. Hg	78·300	78·840	77·720	77·179	76·603	78·464	78·650
H, cm. oil	26·740	9·030	22·280	25·713	26·776	8·984	26·820
t, temp. tubes	16°·7 C.	16°·7 C.	16°·7 C.	16°·7 C.	16°·7 C.	21°·62 C.	21°·4 C.

As in the case of the experiments on air, the percentage decrease in the flow per degree increase in t was measured. It was found to amount to 0·299 per cent. for H = 26·82, and 0·518 per cent. for H = 8·984.

(27) *The Calorimetric Experiments.*—The method of performing the experiments was similar to that employed in the case of air; only the leads Qp were, however, used for carrying the current. The values of the quantity (a) involved in the correction for the heating effect of the leads were assumed to be the same as those for air, both in the cases of the large and small flows, this assumption being justified by the fact that the temperature conditions were the same, and the quantities of energy supplied per second in the corresponding flows for air and CO_2 were practically the same.

In view of the large variation of the specific heat of CO_2 with temperature, the correction to be applied when the two runs from which a value of the specific heat was deduced were performed at slightly different temperatures was more important than in the case of air, so a preliminary value of the temperature coefficient was obtained which served for the purpose of calculating the corrections.

The complete tables of the observations are preserved in the archives, but the following abridged tables show the main quantities upon which the values of the specific heat depend. The tables correspond to those given on pp. 226–228 for air; two additional columns are added, one to denote the number of the experiment and one to denote the number of the bottle used in that experiment, and also whether it was full (F) or half empty (E) at the commencement of the run.

Instead of alternating the quick and slow flows, two or three runs with large flows were generally performed first, and followed by two or three runs with small flows, in order to economise gas. In such cases, if one of the large and one of the small flows were performed with fresh bottles, while another pair were performed with half empty bottles, two values of the specific heat were calculated, one from the pair with fresh bottles and one from the pair with half empty bottles. In this way each value of the specific heat was calculated from two runs in which the composition of the gas was practically the same. This is an advantage, for although the presence of a little air in the CO_2 only affects the measured value of the specific heat to a very small extent, the error becomes magnified if the composition of the gas differs in the two flows.

(28) Abridged Tables for the Main Calorimetric Experiments on Carbon Dioxide.

Table I.—Air Temperature.

Date.	Experiment.	Bottle.	Flow, Q.	Rise, $\delta\theta$.	Watts, CE.	Mean temperature.	h.	Specific heat.	Specific heat at 20° C.	e.
										per cent.
Aug. 21 .	1	1 F	0·96379	5·3438	4·4786	19·32	0·02322 at 19°·32 C.	0·20226 at 19°·32 C.	0·20242	+0·32
	4	2 F	0·42748	5·2275	2·0126	19·86				
	2	1 E	0·96308	5·2700	4·4221	19·44	0·02577 at 19°·44 C.	0·20204 at 19°·44 C.	0·20217	+0·18
	3	1 E	0·42397	5·3208	2·0430	19·66				
Sept. 6 .	1	4 F	0·95284	5·3236	4·4086	19·74	0·02802 at 19°·74 C.	0·20088 at 19°·74 C.	0·20094	−0·42
	3	4 F	0·42756	5·3294	2·0666	20·86				
	2	5 E	0·95206	5·3169	4·4075	19·74	0·02653 at 19°·74 C.	0·20163 at 19°·74 C.	0·20169	−0·05
	4	5 E	0·42768	5·3265	2·0652	20·86				

Mean values for the specific heat at 20° C. = 0·20180 cal. per gr. degree.

Table II.—Steam Temperature.

Date.	Experiment.	Bottle.	Flow, Q.	Rise, $\delta\theta$.	Watts, CE.	Mean temperature.	*h*.	Specific heat.	Specific heat at 100° C.	*e*.
										per cent.
Aug. 30 .	1	2 E	0·42863	5·6324	2·4764	101·54	0·04398 at 102°·04 C.	0·22136 at 102°·04 C.	0·22087	−0·04
	2	2 E	0·42839	5·6314	2·4779					
	3	2 E	0·42799	5·6295	2·4779					
	4	3 E	0·91347	5·5403	4·9251	102·04				
	5	3 E	0·91333	5·5364	4·9237					
Sept. 7 . .	1	F	0·42510	5·5940	2·4525	101·67	0·04494 at 102°·2 C.	0·22165 at 102°·2 C.	0·22112	+0·07
	3	F	0·89011	5·5690	4·8431	102·20				
	2	E	0·42517	5·5890	2·4519	101·67	0·04535 at 102°·2 C.	0·22154 at 102°·2 C.	0·22101	+0·02
	4	E	0·89004	5·5642	4·8385	102·20				

Mean value for the specific heat at 100° C. = 0·22097 cal. per gr. degree.

Since all the measurements on August 30 were made with gas from a half-spent bottle, the specific heat could be most simply calculated by taking the mean values of CE/$\delta\theta$ and Q from the set of experiments 1, 2, 3, and combining them with the mean values from the set 4, 5. For this reason the value of S, calculated from the experiments on August 30, is given double weight in calculating the mean value of S.

The determinations of the specific heat made with bottles which were full at the commencement of the runs do not show sufficiently definite deviations from those made with bottles which were nearly empty to warrant grouping them separately; it is interesting to observe, however, that the effect of the presence of air can occasionally be detected in the observations, for example, in the case of the experiments performed on August 21, the observations for Experiment 1 were taken after the bottle had been running for 40 minutes, while those for Experiment 2 were taken after it had been running about 20 minutes longer. If the values of CE/$\delta\theta$ are calculated, it will be seen that in Experiment 2 the value of CE/$\delta\theta$ has increased while that of Q has decreased, indicating that as the CO_2 became purer, the specific heat increased; the fact that the value of S calculated from 1 and 4 does not come out less than the value calculated from 2 and 3 may be due to the bottle 2 in Experiment 4 containing CO_2, which was less pure than that contained by bottle 1 in Experiment 1.

(29) *Variation of the Specific Heat at Constant Pressure with Pressure.*—From the equation on p. 230 it can be shown the $(\partial s/\partial p)_\theta = n\,(n+1)\,c/\theta$. Prof. Callendar has shown that* for CO_2, $n = 2$, $c_0 = 4{\cdot}56$. Hence at 20° C. $(\partial s/\partial p)_{20} = 0{\cdot}0811$, or if S be expressed in calories per gr. degree C., and 1 cm. of Hg be taken as the unit of pressure $(\partial s/\partial p)_{20} = 0{\cdot}000026$, corresponding to a change of 0·01 per cent. in the value of S for an alteration of pressure of 1 cm. of mercury. At 100° C. the effect is even smaller, and thus it is not necessary to take account of the effect of fluctuations of the atmospheric pressure on the specific heat.

(30) *Further Corrections.*—To the above mean values of the specific heat the corrections mentioned on pp. 229 and 230 remain to be applied. Correction (1) amounts to 6 parts in 10,000 at 20° C. and is additive. The value at 100° C. is 1·5 parts per 1000 and is additive. Correction (2) in the case of CO_2 amounts to an additive correction of 4·8 parts in 10,000. Corrections (3), (4), and (5) form the same percentage of the value of S as in the case of air, and amount to a subtractive correction of 0·2 parts in 10,000. Hence the corrected values of the specific heat in terms of the calorie at 20° C. are

S = 0·20202 cal. per gr. degree at **20° C.**, **S = 0·22141** cal. per gr. degree at **100° C.**

It is interesting to observe that, although the above values are so much greater than those found by Regnault and Wiedemann, the percentage variation of the specific heat with temperature works out to a value intermediate between the values found by those investigators. This is only what might be expected, for the criticism given on p. 231, though affecting the absolute values of the specific heats, would not greatly affect the temperature coefficient.

(31) *Comparison of the Results with the Theoretical Values.*—It is possible to make a comparison of the above results with Joly's value for s in a manner similar to that adopted on p. 230 for air. Joly performed two sets of experiments. The first of these gave s as a function of the absolute density (ρ) in the form $s = 0{\cdot}16577 + 0{\cdot}2064\rho$. The second gave $s = 0{\cdot}1650 + 0{\cdot}2125\rho + 0{\cdot}340\rho^2$, the experiments referring to a mean temperature of 55° C. In order to obtain the true value of s_0 it will, perhaps, be advisable to take the mean of the two values given by the above equations, for, although Joly considered his second set of experiments the more reliable, the first set applied more particularly to the lower pressures.

Thus we obtain for s_0 the value 0·16538 cal. per gr. degree at 55° C. Correcting this value for the fact that Joly used the value 536·7 cal./gr. for the latent heat of steam, we obtain $s_0 = 0{\cdot}16645$, on the assumption that L = 540·2 cal./gr. This value is expressed in terms of the calorie at 20° C. If we assume a linear law for the variation of S with temperature over the range from 20° C. to 100° C., my own observations give, for the value of S at 55° C., S = 0·21050 in terms of the calorie at 20° C.

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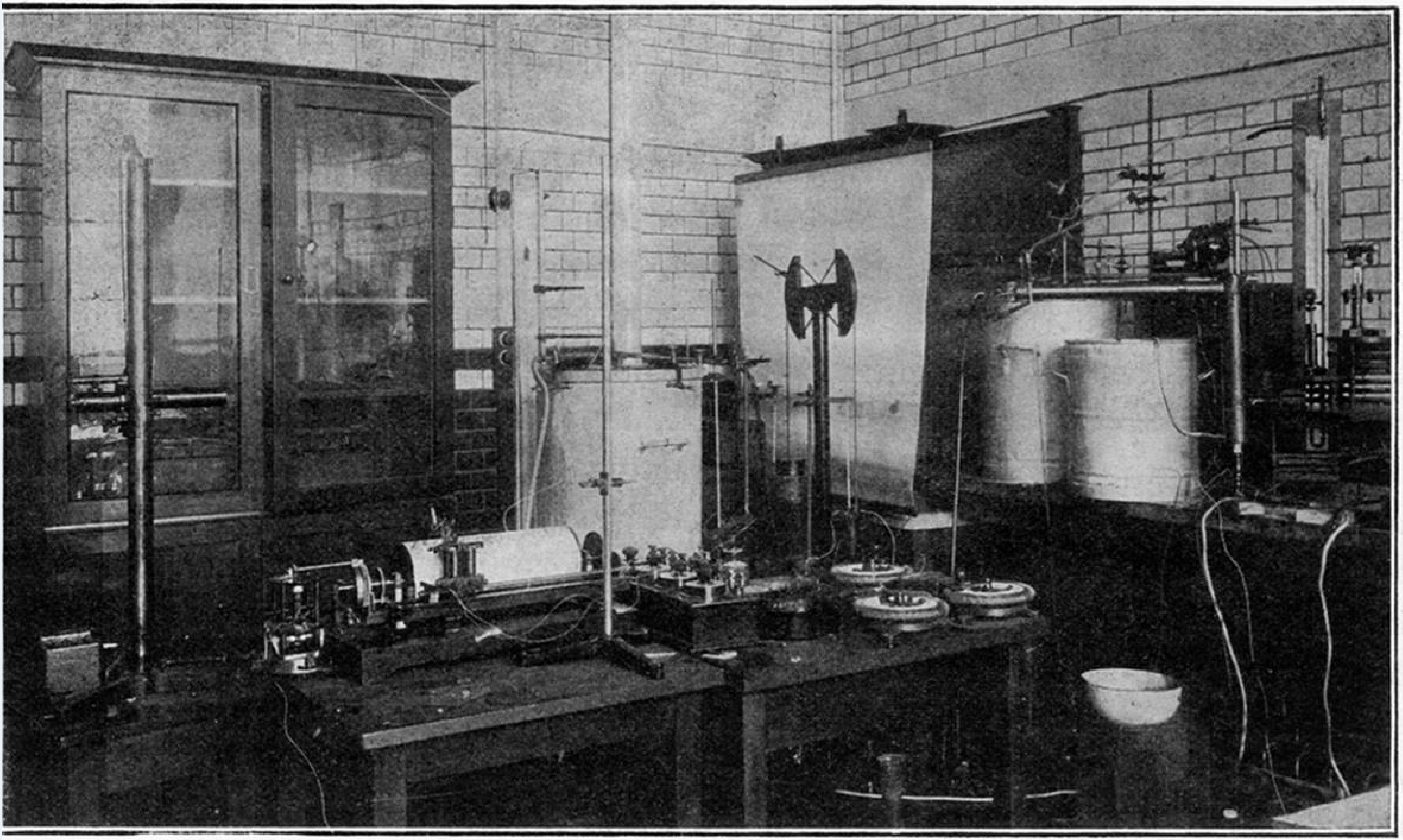
* 'Phil. Mag.,' S. 6, vol. 5, p. 77, January, 1903.

The value of $S-S_0$ may be obtained from the equation $S-S_0 = n(n+1)\,cp/\theta$. Assuming $n = 2$, $c_0 = 3{\cdot}76$, $p = 76/75$, we have $S-S_0 = 0{\cdot}00113$ cal. Hence $S_0 = 0{\cdot}20937$ cal. per gr. degree. Adding the gas constant $R = 0{\cdot}0450$ for CO_2 to JOLY's value $s_0 = 0{\cdot}1665$, we obtain $S_0 = 0{\cdot}2115$, which differs from the value deduced above by 1·0 per cent. of the value of S. The agreement is as good as can be expected, for it is hardly legitimate to assume a linear law for the variation of S over the range 20° C. to 100° C. when the variation over that range amounts to 10 per cent. of the value of S. Further, the two values of s_0 obtained from JOLY's experiments show a lack of agreement amounting to 0·5 per cent. of their values.

The following table gives the approximate values of the specific heat of carbon dioxide at 50° C., deduced from the observations of various experimentalists :—

REGNAULT.	E. WIEDEMANN.	J. JOLY.	HOLBORN and HENNING.	SWANN.
0·2008	0·2060	0·2113	0·2095	0·2093

The last three are in very good agreement, but the rate of increase given by HOLBORN and HENNING is only 0·0133 for 100° C. in place of 0·0240 by the present method. REGNAULT finds the increase 0·0275, and WIEDEMANN 0·0217.



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