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Phil. Trans. R. Soc. Lond. A 1894 **185**, 961-981
doi: 10.1098/rsta.1894.0017

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XVII. *On the Specific Heats of Gases at Constant Volume.—Part III. The Specific Heat of Carbon Dioxide as a Function of Temperature.*

By J. JOLY, M.A., Sc.D., F.R.S.

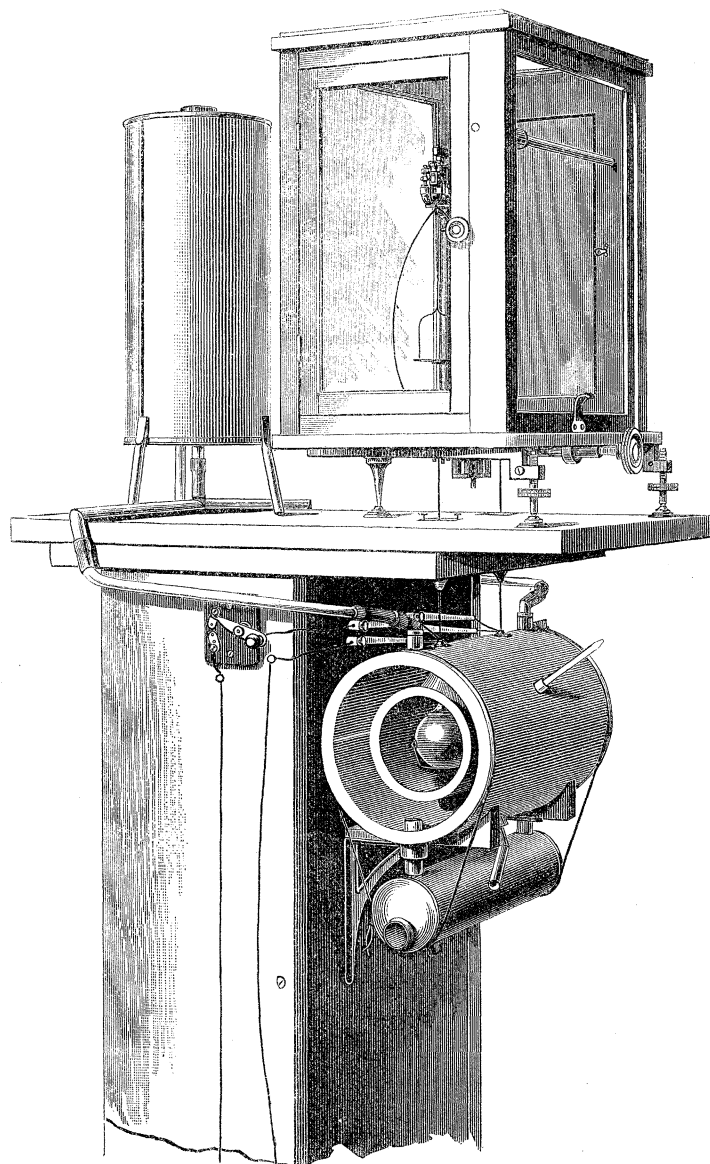
Received March 9,—Read April 26, 1894.

THE question of the dependence of the specific heat of carbon dioxide upon its density having been investigated, so far as is described in Part II., the further question remained over as to whether the specific heat of a gas is dependent upon the range of temperature over which the gas is heated. The question was evidently within the power of the steam calorimeter to answer, provided arrangements were made for varying the lower limit of temperature—the initial temperature. To vary the upper limit by resorting to vapours other than steam would, on the large scale upon which operations were being conducted, have been costly and troublesome, although not attended with any inaccuracy, as the experiments of WIRTZ* on the Latent Heats of several vapours, determined by the method of condensation, appear to show. It is to be observed, indeed, that the use of vapours other than water would allow of operations being conducted upon smaller quantities of the gas, as it would be easy to find liquids whose vapours possessed a latent heat one-half or one-fourth as great as that of water; and a construction necessitating but little loss of vapour at each experiment could be easily contrived. In this case, also, it would be necessary to provide a means of varying the initial temperature. Chiefly on the grounds of expense I decided upon the use of steam in conjunction with a means of altering the initial temperature. It appeared probable, too, that the alteration of the initial temperature between 10° and 100° would disclose the chief points of interest in the case of the gas under consideration, the critical temperature lying within this range.

A means of altering the initial temperature was obtained by conferring such a form upon the steam calorimeter as would permit of the circulation of the vapour of a suitable liquid, boiling under atmospheric pressure, around an inner chamber containing the active and the idle vessels till these had acquired the temperature of the vapour. Steam could then be admitted directly into the inner chamber; the resulting precipitation upon the vessels being that due to the range defined by the boiling-point of the liquid and the boiling-point of water. The accompanying figure (from a

* 'Ueber eine Anwendung des Wasserdampfcalorimeters zur Bestimmung von Verdampfungswärmen.' KARL WIRTZ. Leipzig, 1890.

photograph) shows the details of construction in so far as there is departure from the general arrangements of the differential steam calorimeter, as described in the 'Proc. Roy. Soc.,' vol. 47, p. 218.



The lids of both the inner and outer chamber are shown removed at the end nearest the spectator, so that the active sphere containing the gas can be seen hanging in its place. From it depends the light platinum catch-water. The calorimeter can be opened in a similar manner at the remote end, to facilitate removing the idle sphere and drying the walls. All is made of very light brass, but both the inner and outer drums are flanged by stiff L-pieces on the ends, which are ground true and smooth, so that the lids or covers (which are of thin brass, "dished"

outwards to confer stiffness), with corresponding flanges, can tightly close the inner and outer chambers. To make a joint impervious to the vapour in the space between the chambers it was found requisite to lay on a flat rubber ring with rubber cement and compress these between the flanges by five screw-clamps placed equidistantly around each joint. In the case of the use of ether a lutant had to be used instead of the rubber. After many trials it was found that one made of whitening and glycerine mixed to a stiff consistency gave the best results, glycerine being almost insoluble in ether. In the upper side of the inner drum, over each sphere, a wide opening closed by a light conical roof of brass is provided. One is partially seen in the illustration. This cone is prolonged by a tube about 1 cm. in diameter, which finally emerges through the top of the outer drum. Here it is ground to a smooth horizontal edge and fitted with the loose adjustable cone and self-adjusting disk, which permits the free passage upwards of the wire through a very fine opening, as described in the 'Proc. Roy. Soc.,' *loc. cit.* The edges of the wide openings in the roof of the inner drum are turned a little upwards all around into the cone, so that water drops, running down the latter, will not fall off upon the spheres, but be conducted, as by a gutter, to the lowest point of the intersection of the cone with the cylinder and then overflow harmlessly down the wall of the drum.

Steam is admitted into the inner chamber by a wide central orifice 3.5 cm. in diameter at the back of the drum, the steam-pipe being arranged as described in the 'Proc. Roy. Soc.,' *loc. cit.*, and concealed from view in the figure by the wooden stand which supports the instrument. The escape of the air replaced by the steam takes place through a central opening (1.7 cm. diameter) at the bottom of the drum, a tube leading it directly outside the calorimeter. When the air has been expelled and steam is seen to follow it, the opening is narrowed by insertion of a cork carrying a brass tube, shown in the figure, of about 8 mm. bore. This is bent and can be turned outwards, or to one side, to direct away from the balance the continuous outflow, necessary to preserve the slow circulation of steam in the calorimeter. A third central tubulure entering the inner chamber enables a thermometer to be inserted, as shown.

The outer drum has four tubular openings: two below (one at each end) to permit an inflow of the vapour from the boiler attached beneath it, two above to convey the excess of vapour to the condenser which is seen standing behind the balance. This condenser is simply a tin plate cylinder, open at top with a central inner cylinder of thin copper also open at top, and seen rising a little above the level of the outer cylinder. Ice is placed in the annular space between during experiment. The leading tubes are of such width and so sloped that the returning current of condensed vapour will not choke the tubes, but flow freely back into the vapour jacket and boiler beneath. It is important that these conducting tubes should be of glass so that the heating of the boiler can be adjusted to produce the least current

into the condenser. The condenser was found to act so perfectly that when a loose cork was placed closing the inner tube of copper, and there was no leak at the flanges of the calorimeter, the circulation of ether, acetone, or alcohol could be continued for hours with little attention and with so little loss of the material as to preserve the room almost free of odour. My arrangements did not attain to this state of perfection, however, till some costly experience had been acquired. As application of a burner directly beneath the boiler containing ether, acetone or alcohol, would have been attended with much risk, the arrangement was adopted of heating it by a current of steam derived from a small subsidiary steam boiler placed some 2 metres distant. This was found to be a very simple and manageable arrangement. The steam boiler had a small valve which could be set so that the steam could be let escape more or less directly into the air, a tube sloped upwards from the boiler to the vaporizer beneath the calorimeter, entering at the remote end of the heating tube (or "furnace") in the figure. The near end was narrowed by a glass tube in a cork, bent downward. It was possible to regulate the supply of steam so that a bead of water in this tube remained pulsating for two or more hours without being completely displaced, and once started, the whole system of circulating steam and vapour required but little attention. I had, however, many vexatious failures from leakage into the inner chamber, which for long I naturally attributed to bad flange joints, till ultimately I traced it to a small leak in the soldering of one of the central tubes. I may observe indeed, that the presence of a small quantity of vapour within, whether ether, acetone or alcohol, seemed to have little or no effect as a cause of error. As the result of my entire experience, however, with this mode of heating, I think a water jacket and thermostatic arrangement would probably give less trouble and certainly entail less expense. It would in this case only be necessary to provide sufficiently large valves in the bottom of the outer drum to permit of the rapid removal of the water immediately before or after the admission of steam.

The switch and electrical connection permitting of the heating of the orifices for the suspending wires during experiment, are seen in the figure as well as the platinum spirals (hardly distinguishable in the figure) and forceps holding them. The balance above is a short-beam (14 cms.) of Sartorius, and weighs accurately to $\frac{1}{10}$ milligramme when carrying the spheres. The mode of suspension of the spheres from the balance is as described in the 'Proc. Roy. Soc.,' *loc. cit.*

Four intervals of temperature were adopted for the experiments: air temperature to 100° ; 35° (B.P. of ether) to 100° ; 56° (B.P. of acetone) to 100° ; and 78° (B.P. of alcohol) to 100° . The procedure was as follows in making the experiments. A certain weight of carbon dioxide being enclosed within the sphere, this is hung on the calorimeter; both outer and inner drums closed, and after some hours the air temperature in the calorimeter and the barometric pressure determined. The equilibration of the balance is now attended to and particulars noted down. Steam from the small boiler is then led into the steam 'furnace' of the evaporator, in which

ether, alcohol, or acetone, as the case may be, is contained. In a few minutes the steam current raises this to boiling. Ice is placed in the condenser, and the boiling urged till the back-streaming of the condensed vapour is visible in the glass tubes leading to the condenser. The burner beneath the boiler and finally the discharge valve upon it are now adjusted, till the streaming in the tubes progresses at a slow rate. At the expiration of 40 minutes or thereabouts, the thermometer in the inner chamber rises to a temperature but little below the B.P. of the liquid in use. The final stationary temperature is not attained, however, till one-and-a-half or two hours have elapsed, generally. The balance above is now set vibrating for ten or fifteen minutes and all is ready for admitting steam. At this stage the balance probably shows a slight want of equilibrium due to distension under the increased pressure of the active sphere and also, perhaps, to some leakage of vapour into the inner chamber. This loss of equilibrium is, however, not attended to, the reference-state of equilibrium being taken as the state at air temperature.

Steam is got up in the large boiler feeding the calorimeter while the balance is vibrating, and when the boiler has been vigorously steaming for some minutes the balance is brought to rest, the thermometer withdrawn from the calorimeter, and one for reading steam temperatures inserted in its stead. The air-escape tubulure of the calorimeter being uncorked, the cork stopper closing the large steam entrance at the back is withdrawn, and the steam pipe rocked across into its place, so that steam pours rapidly into the calorimeter. The steam current almost immediately appears flowing out through the air-escape tubulure, and this current is now moderated by inserting the narrow leading tube. The steam supply to the vaporizer is next to be cut off, and the switch moved to put on the current in the spirals. All these operations only take a few seconds, and are almost automatically performed, after some training, by the experimenter; so that some thirty seconds after steam is turned into the calorimeter he can already be observing the behaviour of the balance. Two minutes to two-and-a-half minutes will complete the heating of the vessels and gas, but the even swinging of the balance is observed till the completion of the fifth minute. Then all is to be again cooled as quickly as possible, for the pressure attained in some cases is so high and so sudden (possibly rising from 47 to 102 atmospheres in the space of a minute or less), that it is desirable to relieve the sphere of the excessive stress as soon as possible. The drying of the calorimeter should be effected while it is still hot.

As may be imagined, it is difficult to effect more than one experiment in the course of a day, and thus the completion of many series of experiments demands much time and labour. But except a more expeditious method of altering the initial temperature is devised the delay seems unavoidable.

It will be apparent that the weighings are two in number for each experiment. The first gives the equilibration of the vessels when in air at known temperature and pressure. The second when in steam at known temperature and pressure, and when a certain weight of steam has been precipitated upon each. These weighings are

evidently unaffected by any buoyancy effect due to a small quantity of the jacketting vapour leaking in—as already indicated—and so facilitate calculations having reference to displacement errors.

To correct for the unequal thermal capacities of the spheres over the several ranges, it was thought best to calculate the correction upon the basis of experiments over the widest range of temperature. Table I. contains the experiments upon the spheres between air temperature and steam temperature.

TABLE I.—Correction for Unequal Thermal Capacity of Spheres.

t_1 .	t_2 .	$t_2 - t_1$.	w .
11·89	100·16	88·27	0·0245
11·61	100·24	88·63	0·0243
12·07	100·18	88·11	0·0251
13·30	99·88	87·58	0·0251
Means		88·15	—0·02475

The mean result is a deductive correction of 0·02475 over 88·15 degrees. To determine the proper deduction to be applied to other intervals of temperature it is necessary first to make a correction by deducting a constant effect due to unequal displacement, and thus arrive at the true calorific effect due to heating through 88·15 degrees. The external volume of the active sphere is 105·595 cub. centims., that of the idle sphere but 99·810 cub. centims. (see Part II., pp. 944 and 945), this gives a buoyancy correction of —0·0035 gm.; leaving a calorific effect of 0·0212. Assuming BEDE's results for the specific heat of copper, we have the formula $C = 0·0892 + ·000065 t^\circ$, by which to calculate the deduction proper to other ranges of temperature. To this the displacement effect proper to each case must be added. The "correction for spheres" at base of each table is got in this manner.

Regarding other corrections, the remarks made in Parts I. and II., and the system of tabulation adopted in Part II., are adhered to. The initial temperatures are, of course, the boiling-points of the liquids used in jacketting, and P_1 is the pressure at that temperature, due to W grammes of gas. The pressure for the experiments of Tables II. to XVI. inclusive are obtained from a plotting of AMAGAT's results against density. The mean pressure, P , is obtained by adding one atmosphere to the value read directly from the curve, as explained in Part II. The pressures obtaining in the remaining experiments, Tables XVII. to XX., are obtained from ANDREWS' results.

The purity of the gas used was tested on a sample released from the sphere when reducing the mass under experiment. 66 cub. centims. were absorbed by caustic

potash, and a volume of 0.11 cub. centim. unabsorbed gas remained in the tube. The impurity is therefore about one part in 550 by volume. The drying was effected by filling from the bottle through an iron drying tube containing fresh phosphorus pentoxide. The one sample of gas was used throughout the several series of experiments; known weights being released at intervals.

The thermometers were made by Messrs. NEGRETTI and ZAMBRA, and corrected at Kew. They were four in number, to secure open scales: 0° to 20° , 20° to 50° , 50° to 70° , and 70° to 100° . In the following tables of sets of experiments it will be understood that the initial temperature of 78° is obtained by a jacket of the vapour of absolute ethyl alcohol boiling under atmospheric pressure; the temperature, 56° by acetone vapour, 35° by pure ether; the lowest initial temperature being air temperature. It will be noticed that the density given in the several tables varies to some extent even with the same value of W . This is due to the thermal-pressure corrections on the volume of the vessel varying with the range.

The tables give, in addition to the initial and final temperatures, the range and the latent heat of steam at t_2 . The values in the column " ω " are the gross effects produced upon the balance. The portion of this effect due to the inequalities of volume and thermal capacities of the vessels is given beneath, as well as the sum of all other corrections, needing notice, due to the dynamical or buoyant effects set up by the gas in the active sphere. ϖ is the balance of ω , or precipitation, due to the calorific capacity of the quantity, W , of gas, at constant volume, over the range obtaining. On this the mean specific heat over the range is calculated.

TABLE II.— $W = 17.6658$. Mean Density = 0.1971.
Mean Pressure = 97 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	ω .
77.77	99.55	536.9	21.78	0.1554
77.97	99.82	536.7	21.85	0.1547
77.77	99.55	536.9	21.80	0.1557
77.84	99.64	536.8	21.80	0.1553
Correction for spheres = -0.00886 .				
Other corrections = -0.00054 . $\varpi = 0.1459$.				
Deduced specific heat = 0.20337.				

TABLE III.— $W = 17.6658$. Mean density = 0.1973.
Mean Pressure = 85 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
33.76	99.45	536.9	65.69	0.4801
33.95	99.56	536.9	65.61	0.4789
34.35	99.68	536.8	65.33	0.4759
34.02	99.56	536.9	65.54	0.4783
Correction for spheres = -0.0180 . Other corrections = -0.0013 . $\varpi = 0.4592$.				
Deduced specific heat = 0.21294.				

TABLE IV.— $W = 17.6658$. Mean Density = 0.1974.
Mean Pressure = 79 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
13.35	99.47	536.9	86.12	0.8733
13.40	99.45	536.9	86.05	0.8796
12.53	99.87	536.7	87.34	0.9061
12.94	99.72	536.8	86.78	0.8895
12.52	99.39	537.0	86.87	0.9008
12.03	99.95	536.6	87.92	0.9224
12.79	99.64	536.8	86.85	
Correction for spheres = -0.0244 . Other corrections = -0.00124 . $\varpi = 0.8701$.				
Deduced specific heat = 0.30442.				

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TABLE V.— $W = 16.1147$. Mean Density = 0.1802 .
Mean Pressure = 75 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
12.66	100.14	536.5	87.48	0.7589
13.30	100.05	536.5	86.75	0.7306
12.95	100.16	536.5	87.21	0.7416
13.30	100.04	536.5	86.74	0.7307
13.37	99.88	536.6	86.51	0.7298
13.12	100.05	536.5	86.94	0.7383
Correction for spheres = -0.02447 . Other corrections = -0.00134 . $w = 0.7129$.				
Deduced specific heat = 0.27299 .				

TABLE VI.— $W = 16.1147$. Mean Density = 0.1800 .
Mean Pressure = 91 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
77.96	99.75	536.7	21.79	0.1413
77.67	99.40	537.0	21.73	0.1415
77.97	99.77	536.7	21.80	0.1414
77.87	99.64	536.8	21.77	0.1414
Correction for spheres = -0.0088 . Other corrections = -0.00055 . $w = 0.1321$.				
Deduced specific heat = 0.20212 .				

TABLE VII.— $W = 16.1147$. Mean Density = 0.1800 .
Mean Pressure = 86 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
56.06	100.04	536.5	43.98	0.2820
55.93	99.77	536.7	43.84	0.2830
56.11	99.97	536.6	43.86	0.2865
56.43	100.25	536.4	43.82	0.2857
56.13	100.01	536.6	43.88	0.2843
Correction for spheres = -0.0144 . Other corrections = -0.00107 . $\varpi = 0.2689$.				
Deduced specific heat = 0.20405 .				

TABLE VIII.— $W = 16.1147$. Mean Density = 0.1801 .
Mean Pressure = 80.5 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
34.96	100.01	536.5	65.05	0.4187
34.76	99.64	536.8	64.88	0.4230
35.07	99.86	536.6	64.79	0.4235
35.19	99.95	536.5	64.76	0.4205
35.65	100.06	536.5	64.41	0.4212
35.13	99.90	536.6	64.78	0.4214
Correction for spheres = -0.0191 . Other corrections = -0.0015 . $\varpi = 0.4008$.				
Deduced specific heat = 0.20602 .				

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TABLE IX.— $W = 11.0416$. Mean Density = 0.1240 .
Mean Pressure = 68.5 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
78.26	100.20	536.4	21.94	0.0953
78.32	100.12	536.4	21.80	0.0953
77.96	99.77	536.7	21.81	0.0954
78.18	100.03	536.5	21.85	0.0953
Correction for spheres = -0.00870 . Other corrections = -0.00141 . $\varpi = 0.0861$.				
Deduced specific heat = 0.19146 .				

TABLE X.— $W = 11.0416$. Mean Density = 0.1240 .
Mean Pressure = 65 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
56.48	100.15	536.4	43.67	0.1846
56.56	100.16	536.4	43.60	0.1849
56.59	100.20	536.4	43.61	0.1891
56.53	100.06	536.5	43.53	0.1852
56.29	100.00	536.5	43.71	0.1857
56.49	100.11	536.4	43.62	0.1859
Correction for spheres = -0.0142 . Other corrections = -0.00055 . $\varpi = 0.1713$.				
Deduced specific heat = 0.19080 .				

TABLE XI.— $W = 11.0416$. Mean Density = 0.1241 .
Mean Pressure = 61 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
34.27	99.93	536.5	65.66	0.2790
34.78	99.99	536.5	65.21	0.2813
35.42	100.25	536.3	64.83	0.2775
35.58	99.86	536.6	64.28	0.2786
35.12	100.05	536.5	64.93	0.2785
35.05	100.02	536.5	64.98	0.2790
Correction for spheres = $- 0.01910$. Other corrections = $- 0.00070$. $\omega = 0.2591$.				
Deduced specific heat = 0.19374 .				

TABLE XII.— $W = 11.0416$. Mean Density = 0.1242 .
Mean Pressure = 57.5 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
6.87	100.25	536.3	93.38	0.4312
5.93	100.32	536.3	94.39	0.4561
6.33	100.08	536.5	93.75	0.4435
6.51	99.73	536.7	93.22	0.4356
6.31	99.88	536.6	93.57	0.4434
6.39	100.05	536.5	93.66	0.4420
Correction for spheres = $- 0.02607$. Other corrections = $- 0.00086$. $\omega = 0.4150$.				
Deduced specific heat = 0.21530 .				

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TABLE XIII.— $W = 7.0537$. Mean Density = 0.0800.
Mean Pressure = 41.5 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
6.89	100.26	536.3	93.37	0.2506
7.91	100.52	536.2	92.62	0.2513
7.92	100.41	536.2	92.49	0.2505
8.70	100.27	536.3	91.57	0.2491
8.75	99.95	536.5	91.20	0.2476
8.03	100.28	536.5	92.25	0.2498
Correction for spheres = - 0.02657. Other corrections = - 0.00068. $\varpi = 0.2235$.				
Deduced specific heat = 0.18427.				

TABLE XIV.— $W = 7.0537$. Mean Density = 0.0799.
Mean Pressure = 44.5 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
35.62	100.37	536.3	64.75	0.1757
36.11	100.22	536.4	64.11	0.1748
36.05	100.10	536.4	64.05	0.1749
35.01	100.40	536.2	65.39	0.1765
35.70	100.27	536.3	64.57	0.1755
Correction for spheres = - 0.01910. Other corrections = - 0.00047. $\varpi = 0.1559$.				
Deduced specific heat = 0.18357.				

TABLE XV.— $W = 7.0537$. Mean Density = 0.0799.
Mean Pressure = 46 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
56.34	100.24	536.3	43.90	0.1198
56.78	100.45	536.2	43.67	0.1200
56.88	100.39	536.2	43.51	0.1174
57.05	100.58	536.1	43.53	0.1185
56.89	100.41	536.2	43.52	0.1170
56.79	100.41	536.2	43.62	0.1185
Correction for spheres = - 0.01430. Other corrections = - 0.00040. $\sigma = 0.1038$.				
Deduced specific heat = 0.18120.				

TABLE XVI.— $W = 7.0537$. Mean Density = 0.0799.
Mean Pressure = 48 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
78.06	100.25	536.3	22.19	0.0630
78.04	100.01	536.5	21.97	0.0628
78.25	100.12	536.4	21.87	0.0627
78.22	99.97	536.5	21.75	0.0626
78.14	100.09	536.4	21.94	0.0628
Correction for spheres = - 0.00880. Other corrections = - 0.00021. $\sigma = 0.0538$.				
Deduced specific heat = 0.18635.				

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TABLE XVII.— $W = 3.9510$. Mean Density = 0.0457 .
Mean Pressure = 25.7 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
11.50	99.55	536.8	88.05	0.1404
10.98	99.82	536.6	88.84	0.1413
11.58	99.85	536.6	88.27	0.1406
11.35	99.74	536.7	88.39	0.1406
Correction for spheres = -0.02487 . Other corrections = -0.00033 . $\pi = 0.1154$.				
Deduced specific heat = 0.17735 .				

TABLE XVIII.— $W = 3.9510$. Mean Density = 0.0456 .
Mean Pressure = 28 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
56.21	99.85	536.6	43.64	0.0706
56.56	100.05	536.5	43.49	0.0692
56.73	100.19	536.4	43.46	0.0713
56.85	100.27	536.3	43.42	0.0711
56.84	100.25	536.3	43.41	0.0706
56.88	100.11	536.4	43.23	0.0718
56.68	100.12	536.4	43.44	0.0708
Correction for spheres = -0.01420 . Other corrections = -0.00024 . $\pi = 0.0564$.				
Deduced specific heat = 0.17628 .				

TABLE XIX.— $W = 3.9510$. Mean Density = 0.0456.
Mean Pressure = 26.8 Atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
34.66	100.15	536.4	65.49	0.1031
34.55	99.55	536.8	65.00	0.1027
35.69	99.96	536.5	64.27	0.1036
35.35	99.72	536.7	64.37	0.1028
35.06	99.84	536.6	64.78	0.1030
Correction for spheres = - 0.01900. Other corrections = - 0.00033. $\pi = 0.0837$.				
Deduced specific heat = 0.17548.				

TABLE XX.— $W = 3.9510$. Mean Density = 0.0456.
Mean Pressure = 29 atmospheres.

t_1 .	t_2 .	λ .	$t_2 - t_1$.	w .
77.85	99.54	536.8	21.69	0.0394
77.67	99.40	536.9	21.73	0.0395
78.46	100.40	536.2	21.94	0.0380
78.46	100.41	536.2	21.95	0.0391
78.26	100.25	536.3	21.99	0.0387
78.14	100.00	536.5	21.86	0.0389
Correction for spheres = - 0.00899. Other corrections = - 0.00012. $\pi = 0.02981$.				
Deduced specific heat = 0.18516.				

The foregoing experiments are summarized in the next table. Those experiments in which liquid carbon dioxide was present at the initial temperature have the numerical value of the specific heat printed in black.

TABLE XXI.—Summary of Experiments.

Table.	W.	t_1 .	t_2 .	ω .	ρ .	Sp. heat.	Mean P.
II.	17·6658	77·84	99·64	0·1459	0·1973	0·2034	97·0
III.	17·6658	34·02	99·56	0·4592	0·1973	0·2129	85·0
IV.	17·6658	12·79	99·64	0·8701	0·1973	0·3044	79·0
V.	16·1147	13·12	100·05	0·7129	0·1800	0·2730	75·0
VI.	16·1147	77·87	99·64	0·1321	0·1800	0·2021	91·0
VII.	16·1147	56·13	100·01	0·2689	0·1800	0·2040	86·0
VIII.	16·1147	35·17	99·90	0·4008	0·1800	0·2060	80·5
IX.	11·0416	78·18	100·03	0·0861	0·1240	0·1915	68·5
X.	11·0416	56·49	100·11	0·1713	0·1240	0·1908	65·0
XI.	11·0416	35·05	100·02	0·2591	0·1240	0·1937	62·0
XII.	11·0416	6·39	100·05	0·4150	0·1240	0·2153	57·5
XIII.	7·0537	8·03	100·28	0·2235	0·0800	0·1843	41·5
XIV.	7·0537	35·70	100·27	0·1559	0·0800	0·1836	44·5
XV.	7·0537	56·79	100·41	0·1038	0·0800	0·1812	46·5
XVI.	7·0537	78·14	100·09	0·0538	0·0800	0·1863	48·0
XVII.	3·9510	11·35	99·74	0·1154	0·0456	0·1773	25·7
XVIII.	3·9510	56·68	100·12	0·0564	0·0456	0·1763	28·0
XIX.	3·9510	35·06	99·84	0·0837	0·0456	0·1755	26·8
XX.	3·9510	78·14	100·00	0·02981	0·0456	0·1851	29·0

TABLE XXII.—Calculation of Corrections.

Table.	V_{t_1} .	P_1 .	$V_{t_1 P_1}$.	P_2 .	$V_{t_1 P_2}$.	α .	Corr. I.	Corr. II.	Corr. VII.
II.	90·242	90·0	90·408	102·0	90·434	0·072	—0·00	—0·000	+0·000
III.	90·067	65·0	90·185	102·0	90·259	0·096	0·43	15	09
IV.	89·982	47·2	90·069	102·0	90·174	0·137	112	20	27
V.	89·984	47·5	90·073	95·4	90·162	0·116	109	20	52
VI.	90·242	84·5	90·400	95·4	90·420	0·059	123	15	42
VII.	90·156	74·0	90·292	95·4	90·434	0·070	040	15	07
VIII.	90·071	63·0	90·186	95·4	90·249	0·084	077	30	16
IX.	90·243	64·0	90·361	71·0	90·373	0·046	105	20	24
X.	90·158	57·5	90·263	71·0	90·288	0·054	030	Negligible	05
XI.	90·071	51·0	90·163	71·0	90·201	0·063	056	”	10
XII.	89·957	40·5	90·031	71·0	90·087	0·080	080	”	12
XIII.	89·963	31·5	90·026	49·0	90·093	0·047	106	10	24
XIV.	90·073	36·5	90·142	49·0	90·163	0·047	078	10	13
XV.	90·159	41·0	90·231	49·0	90·249	0·045	057	Negligible	09
XVI.	90·243	45·0	90·317	49·0	90·333	0·046	040	”	06
XVII.	89·976	20·4	90·013	29·0	90·028	0·048	021	”	03
XVIII.	90·159	24·8	90·204	29·0	90·211	0·039	043	”	06
XIX.	90·071	22·7	90·112	29·0	90·123	0·043	024	”	03
XX.	90·159	26·9	90·207	29·0	90·211	0·036	033	”	05
							012	”	02

The foregoing experiments are graphically shown in the diagram at the end of this paper. The five lines sloping to the right are equi-density lines, *i.e.*, lines each of which represents the heat capacity of the gas at one special density. For although

the thermal expansion of the spheres, as indicated, introduced slight differences of density into observations over variable ranges of temperature, this effect is so small, as may be seen by referring to the tabular statement of experiments, that experiments upon the one mass of gas may be considered, without introducing sensible error, as being experiments also upon gas of the one constant density. Each of these lines is determined by measuring the initial temperature, above 0° , of experiment horizontally; the condensation in grammes of water (τ)—after all corrections—vertically. The temperatures are numbered from the origin 0° to 100° . At 100° , as initial temperature, there could be no condensation, hence all the lines must pass through this point. As the condensations are set off vertically at the initial temperature, t_1 , of each series of experiments, the slope of the line joining this point to the point 100° on the axis of temperature affords the mean specific heat over the range t_1 to 100° . Hence joining all the points so fixed gives a graphic representation of the behaviour of the gas at the particular density to which the experiments apply when the lower limit of temperature is varying. The dotted lines upon the diagram to Part II. give these same experiments, for the most part, but plotted as specific heats against absolute density.

Looking at the lowest couple of lines, $\rho = 0.0456$ and $\rho = 0.0800$, we see observations connected by a straight line—laid down in fact through the experiments by aid of a straight-edge, and it follows from this—the slope of the line being uniform throughout—that at these densities the variations of specific heat, as the range is varied from about 10° – 100° , 35° – 100° , 56° – 100° , and 78° – 100° , is so small as to have escaped experimental detection or be non-existent. For although the lower of the two densities lies at the limit to which observations could be carried with the arrangements used, and are therefore unsteady in some degree, the higher density allowed of considerable accuracy in the observations, and the uniformity of the line obtained for it, taken in conjunction with the teaching of the lines referring to higher densities—which show a curvature increasing with the density—appears to render it a safe conclusion that at densities below 0.08 the variation of the specific heat with temperature, over the limits 10° to 100° , is very small. Not probably non-existent, however, as there is no reason to suppose any discontinuity in the physical properties of the gas, as its density increases to that of the third line, 0.1240 .

This line, 0.1240 , shows that throughout the specific heat is very slightly variable. The sharp upward curvature at the colder end is due, however, to the presence of a small quantity of the liquid carbon dioxide not evaporated till a temperature of 8° C. was reached, whereas the mean initial temperature was 6.39 (Table XII.). The upper lines more strongly repeat this behaviour. When, also, the actual specific heats are plotted against density, as in the diagram to Part II., it is seen that the dotted line carrying the experiments over the range 35° – 100° lies at the higher densities well below that for the ordinary range, 12° – 100° , and to possess an upward curvature with increasing density. Again, the line for experiments between 57° and 100° lies

still lower; the line for 78° to 100° being lowest. At low densities all these lines tend to converge, as if the specific heat was then unaffected by the difference of range.

As liquid is present at $\rho = 0.124$ from 6° to 8° C., it is to be concluded that in the neighbourhood of these temperatures most of the fall between $6^{\circ}.39$ and 35° is accomplished. We can refer to Part II. for a point about 16° C. The full curve of the diagram, Part II., gives the specific heat at this density, and knowing the weight (11.0416 grms.) affording this density we calculate ϖ and so get the point marked \square . This is a very reliable point, and as will be seen it carries back with uniformity the course of the line at the upper temperatures.

The line for $\rho = 0.124$ is given by the following equation:—

$$\varpi = a(100 - t) + b(100 - t)^2 + c(100 - t)^3,$$

$$\text{where } a = 0.003915; \quad b = -0.00000139; \quad c = 0.0000000375.$$

If these numbers are multiplied by the latent heat of steam and divided by W , *i.e.* by $536.5/11.042 = 48.56$, we get, by differentiating with respect to t , an equation for the specific heat in terms of temperature at the density 0.124:—

$$C_v = a + 2b(100 - t) + 3c(100 - t)^2.$$

where

$$a = 0.19020000,$$

$$b = -0.00006750,$$

$$c = 0.00000182.$$

This, of course, is plotted, virtually, by the inclination of the curve upon the plate, the ordinates all being supposed as lengthened in the ratio 1 to 48.56.

The line above this, $\rho = 0.1800$, shows a rapid upward curvature below 35° ; liquid in fact was present up to $18^{\circ}.5$. Nothing being accurately known as to the specific heat of the saturated vapour, we cannot safely assume anything as to the course of events between the 13° and 35° points. A *theoretical* point obtained from the curve of Part II., at the initial temperature 15° , lies on the prolongation of the experiments at the upper temperature. It is not, however, marked upon the dotted line, as it cannot be relied upon, except it be shown that the variation with temperature of the specific heat of the saturated vapour is at the same rate as that of the superheated vapour.

The following equation, of similar form to the last, gives the inclination of this line with fair accuracy:—

$$C_v = 0.2056 - 2 \times 0.0000819(100 - t) + 3 \times 0.00000133(100 - t)^2.$$

The specific heat is directly given by this for the density 0.180.

With regard to previous theoretical considerations, in reference to the temperature variation of the specific heat of a gas, it has been shown that where a gas departs from BOYLE'S Law in the direction in which carbon dioxide does, there is reason to expect a diminishing specific heat with rise of temperature. This is based upon a thermodynamic equation due to RANKINE.*

$$K_v = C + T \int_a^v \left(\frac{d^2p}{dT^2} \right)_v dV.$$

Integrating the last and variable term in terms of the equation for an imperfect gas,

$$PV = RT - \alpha/TV,$$

the value of K_v becomes

$$K_v = C + 2\alpha/T^2V,$$

α being a constant. It follows that the specific heat at constant volume diminishes with rise of temperature till it attains to the limit C , which is designated by CLAUSIUS the true or real specific heat. From the second term, expressing the variable part, it is easy to calculate that at a density 0.124 the value of the variable term has the value 0.0281 at 50° C., and 0.0223 at 90° C. in thermal units, a fall of 0.0058 thermal unit. Referring to the equation expressing the value of C_v in terms of temperature derived from the experiments upon gas at this density, we find C_v at 50° = 0.1971 and at 90° = 0.1894, or the fall has been 0.0077 thermal unit. The agreement is only approximate. However, the thermodynamic equation and the experiments agree in showing that the variation of specific heat with temperature at low densities is inappreciable; thus the variable term at the density 0.00188 is almost inappreciable in value, and its changes, of course still more so. At 0° C. it has the value 0.0007, at 50° C. the value 0.0004, and at 90° C. 0.0003.

Again, if we evaluate the variable term in the case of the density being 0.0800—the second equi-density line on the plate—it is found that the sensibly rectilinear plotting of the experiments is in agreement with theory. The fall in the specific heat between about 10° and 100° C. calculates, in fact, to be 0.00103. This is a far wider range than the range of mean temperatures in the experiments. The experiments did not cover more than half this range, and must have been competent to show a variation of one part in 2000 upon values of ϖ lying between 0.223 and 0.054 grammes. This was hardly to have been expected. And this applies more forcibly to the lowest line, the density 0.0456.

On endeavouring to apply the thermodynamic equation to the line $\rho = 0.180$, it appeared that it was less agreeable with the experiments. The reason of this is probably to be found in the inapplicability of the formula to serve as the equation of the gas at high pressures. It is, in fact, based upon REGNAULT'S observations. Nor

* 'Thermodynamics,' DE VOLSON WOOD, p. 118

did the more recent one of CLAUSIUS* afford an agreement with the results of experiment. M. SANAN ('Comptes Rendus,' vol. 94, 1882)† has shown that CLAUSIUS' form of the characteristic equation possesses but a limited applicability to carbon dioxide when tested with AMAGAT'S results. It is easy to test this point by calculating for the pressure at the density 0·1800 at some chosen temperature, and comparing with AMAGAT'S results. A deficiency in the value of the pressure given by the formula to the extent of some 12 per cent. is obtained. The close agreement between this line, $\rho = 0\cdot1800$, and the neighbouring one, $\rho = 0\cdot1973$, is, I think, strongly confirmatory of the accuracy of both. Indeed, the quantities of precipitated steam then dealt with are so large that I do not see how serious error could have arisen. I therefore venture to think that they truly represent the variation of the specific heat with temperature at these densities.

* 'Phil. Mag.,' June, 1880.

† See 'The Theory of Heat,' T. PRESTON, p. 422.

