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On the Specific Heats of Gases at Constant Volume. Part II. Carbon Dioxide

J. Joly

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XVI. *On the Specific Heats of Gases at Constant Volume.*—Part II. *Carbon Dioxide.*

By J. Joly, *M.A., Sc.D., F.R.S.*

Received March 9,—Read April 26, 1894.

The present paper is occupied with an experimental investigation into the variation of the specific heat at constant volume of carbon dioxide attending change of absolute density. The investigation is in continuation of a previous one,* in which Carbon Dioxide, Air, and Hydrogen were the subjects of a similar enquiry over low ranges of density. It appeared to me desirable to extend the observations more especially in the case of carbon dioxide, because of the extended knowledge we already possess of its isothermals, and the fact that its critical temperature is within convenient reach. Other physical properties of the gas have also received much attention of recent years. It is also readily procured in a nearly pure state.

The observations recorded in this paper extend, in the one direction, to densities, such that liquid is present at the lower temperature; and in the other, to a junction with the highest densities of the former paper. A plotting of the new observations is in satisfactory agreement with the record of the old. It reveals, however, the fact that the linear nature of the variation of the specific heat with density, deduced from the former results, is not truly applicable over the new, much more extended range of observation. For convenience the chart at the end of this paper embraces the former results, and the present paper is extended to include the entire results on the variation of specific heat with density where the range of temperature, obtaining at each experiment, is approximately the same: that from air temperature to 100° C.

Part III. of this investigation will contain an account of experiments on the variation of the specific heat with temperature when the density is kept constant. The division is for convenience of reference.

The value of Professor Fitzgerald's assistance and advice, and his kindness in giving them to all seeking his help, are so well known, that it is needless to say that this present research owes much to his assistance. He is not, indeed, responsible for mistakes I may have fallen into, but he is to be thanked for saving me from committing many.

The arrangements for carrying out the experiments are essentially the same as

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* 'Phil. Trans.,' A., vol. 182, 1891, pp. 73–117.

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those described in Part I. Some modifications in the structure of the calorimeter, &c., must, however, be noticed.

The differential form of the steam calorimeter was used throughout; the mode of experiment being to compare the calorific capacity of a strong spherical copper vessel, firstly when containing but one atmosphere of the gas, and secondly when charged with the requisite mass of the gas, with that of an idle vessel of closely similar mass and volume. Each of these comparative observations embraced a series of from three to ten experiments, according to the mass of gas operated upon; a larger number being requisite when the mass was small. The identical calorimeter, described in Part I., was used in the present experiments up to the completion of the experiments of Table IX. An improved differential calorimeter was then completed for the requirements of the experiments upon the temperature variation of the specific heat. It was accordingly taken into use, and with it the experiments were completed. As its peculiarities of construction are mainly to render it suitable for the experiments described in Part III., its description is deferred to that paper.

To carry out experiments at the high pressures contemplated, new copper spheres of greater strength than the former ones had to be provided. The dimensions were also reduced, and, what was most important, the brazed equatorial joint entirely dispensed with. This was effected by spinning the entire sphere out of the one piece of copper till the vessel was closed down to an orifice of about 2 centims. in diameter. Into this opening an accurately turned piece of gun-metal was brazed. Still further to diminish the number of joints, this piece of brass was so formed that it constituted the valve seat receiving the steel screw-valve, and carried the connecting nozzle used in filling it.* Several of these vessels were made, designed to have a capacity of about 80 cub. centims., and to be 2 millims. thick in the walls. Assuming the tensile strength of copper to be 2×10^6 grammes per square centimetre, these vessels would possess a bursting strength of some 300 atmospheres. The safe limit would be about 100 atmospheres, which pressure was somewhat exceeded on one occasion. One of these vessels having been chosen for use, its internal and external volume were measured. The external volume was found to be 98·752 cub. centims.; the internal, 83·168. Its mass was 137·00 grammes. The external volume of the idle sphere was found to be 99·810 at 13° C.; and the mass, 135·55 grams.

The active sphere was now tested by putting into it some 12 grammes of carbon dioxide, and heating it in a current of steam for 15 or 20 minutes. It became visibly more truly spherical by this treatment, and a re-determination of its external volume afforded 101·737 cub. centims. at 16° C., showing a stretch of 2·985 cub. centims., probably due principally to a more perfect sphericity. The experiments on the gas were now begun, using a mass of 10·5 grammes. Later on, after the experiments of Table IX., the volumes were again determined. The external gave 101·738 cub. centims. at 16°·7 C., which may be considered identical with the previous result; the

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* See Part I. (*loc. cit.*), p. 78.

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internal volume was 86·127 cub. centims. at 16°·7 C. Comparing these last with the first results, obtained before the testing of the sphere, we find that the first results give a volume of copper of 15·584; the last results, 15·611. The results of the measurements of volume therefore agree satisfactorily, and, for the experiments of Tables I. to XII., the foregoing volumes are adopted.

Upon the completion of the experiments of Table XII., a new series, involving much higher pressures, being entered upon, a preliminary test of the sphere was made with the first charge of CO_2 dealt with. This weighed 18·76 grammes. With this charge the sphere was heated for 15 minutes in steam. There was no leakage whatever, and a determination of the external volume revealed that this had risen to 105·595 cub. centims. If from this the volume of copper, 15·611, is taken, the internal volume is found to be 89·984, a further increase of 3·85 cub. centims. This volume applies to the results given in Table XV., as well as to all those subsequently made, recorded in Part III.; for a last determination of the external volume, at the completion of all the experiments, gave 105·520 cub. centims. at 11°·5 C., showing that there was no further increase. These details are given here connectedly as drawing attention to the necessity of careful observation of the volume of the vessel when making such experiments. Otherwise serious error might be introduced into the calculation of the density of the gas. It would appear as if the change of volume was all along mainly due to change of shape. If drawing of the copper had been going on to any considerable extent, the prolonged and severe strains incident to the experiments of Part III. must have produced a marked increase of volume. No such was measured, however.

The elastic yielding of the vessel was determined by an experiment in which 10·542 grams. of CO_2 at the temperature 16°·3 were released from the sphere, its external volume being accurately determined (by its displacement in water) before and after the release. A loss in buoyancy of 0·089 gramme of water at 16°·3 occurred, which, reduced to cub. centims., gives the shrinkage as 0·0891 cub. centim. due to a decrease of pressure of 44·5 atmospheres. This shrinkage is so small that a mass of gas inserted in the sphere may be determined without correction by simply weighing the vessel before and after filling. Thus, in the above case, the neglected correction upon W for change of displacement in air at 16° and 760 millims. has the value $0·0891 \times 0·00122 = 0·00010$ gramme. As this is the case of a considerable charge of gas, such a correction is evidently negligible.

It is, perhaps, further of interest in connection with the particulars of the vessel employed for holding the gas to observe that there is a precipitation of over 2 grammes of steam due to its own calorific capacity between an air temperature of 10° and steam at 100° C. The experiments, however, show that some 4 or 5 grammes of CO_2 (giving precipitations of about 0·135 and 0·172 gramme over a similar range) may be dealt with, and the specific heat determined readily to about 1 per cent. of accuracy (see Tables VII., VIII., XI., XII.). Experiments on a mass so small as 3 grammes

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(Table IX.) were, however, not so concordant with those recorded in Part I. obtained with the lighter vessel then used. This is not to be wondered at when it is remembered that a 1 per cent. accuracy in the case of dealing with 4 grammes of gas is already a determination closer than one part in 4000 of the total precipitation upon the two vessels in the calorimeter, or one two-thousandth part of that upon the vessel containing the gas.

The carbon dioxide used in the experiments was obtained from the brewery of Messrs. GUINNESS and Co. In the brewery it is removed from the fermenting vats, from a level low down, some 15 or 20 feet below the edge of the vat, which remains filled with the gas. It is then purified by washing with water and treatment with permanganate of soda, and compressed into iron bottles. In use it is best to invert the bottle somewhat, so as to draw from the liquid. The gas used in the earlier experiments had a faint alcoholic smell. Later, gas was supplied to me through the kindness of the head engineer, Mr. GEOGHEGAN, which had no perceptible odour. Derminations of the amount of impurity were frequently made, by absorption with alkaline pyrogallol of some 65 cub. centims. of the gas over mercury. The impurity (air, probably) was in all cases small; at worst, about 1 part in 360 by volume. A series of experiments (Table XII.) was carried out upon gas prepared in the laboratory from pure bicarbonate of soda, and pumped into the sphere with the aid of the mercury pump, described in Part I. This gas contained, according to subsequent determination, an impurity of only one part in 1015 by volume. These experiments reveal no discrepancy with those made upon the less pure gas. It is, indeed, not to be expected that the impurity of one in 360 by volume would produce a perceptible error. In filling the gas into the sphere it was passed through an iron drying tube about 1 centim. in diameter and 35 centims. in length, filled with asbestos and phosphorus pentoxide. It was found that the transfer of the liquid into the sphere was greatly facilitated by cooling the latter with ether poured on muslin placed around it.

The first series of experiments were made upon a charge of 10·542 grammes, which by determination showed an impurity of 1 in 485 by volume. They are contained in the following table, and the succeeding table gives a calorimetric comparison of the empty spheres applicable to the experiments. The mode of estimating the pressure, obtaining and of evaluating the deduction to be made for effects other than that (ϖ) due to the calorific capacity of the gas at constant volume, is given further on, after the experiments have been recorded.

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Table I.—W = 10·542 grammes. Mean Absolute Density = 0·1238. Mean Pressure = 59·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	ω.
16·90	99·92	536·5	83·02	0·3391
16·90	100·04	536·5	83·14	0·3402
16·90	99·98	536·5	83·08	0·33965
Corrections for spheres = − 0·01825. Other corrections = − 0·00087. ϖ = 0·32053.				
Deduced specific heat = 0·19634.				

After these two experiments, the total mass of gas was passed through an equilibrated U-tube containing phosphoric anhydride, with the result that the drying tube lost 1 milligramme in weight. The following experiments afforded the corrections for the spheres given in Table I. The minus sign applied to the numbers in column ω is used to indicate that the excess precipitation was on the active vessel, and hence the correction is subtractive from the apparent result for the gas.

Table II.—Comparison of the Empty Spheres.

t_1.	t_2.	$t_2 - t_1$.	ω.
16·21	99·80	83·59	−0·0190
16·85	99·91	83·06	−0·0176
16·02	99·94	83·92	−0·0187
16·80	99·93	83·13	−0·0181
16·80	99·74	83·94	−0·0181
		83·33	−0·0183

A fresh mass of gas was now introduced, and the experiments contained in Tables III. to IX. made upon this sample, successive quantities being liberated at the conclusion of each series.

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TABLE III.—W = 9·6339 grammes. Mean Density = 0·11325. Mean Pressure = 55·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
16·10	99·41	536·9	83·31	0·3102
16·72	99·30	537·0	82·58	0·3061
15·93	99·49	536·9	83·56	0·3098
15·65	99·41	536·9	83·76	0·3115
16·10	99·40	536·9	83·30	0·3094

Correction for spheres = − 0·02024.
Other corrections = − 0·00072. ϖ = 0·28844.

Deduced specific heat = 0·19298.

TABLE IV.—W = 8·6250 grammes. Mean Density = 0·1016. Mean Pressure = 51·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
16·73	99·39	536·9	82·66	0·2722
15·61	99·69	536·7	84·08	0·2780
16·39	99·74	536·7	83·35	0·2746
15·20	100·02	536·5	84·82	0·2792
15·98	99·71	536·7	83·74	0·2760

Correction for spheres = − 0·02032.
Other corrections = − 0·00062; ϖ = 0·25506.

Deduced specific heat = 0·18955.

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TABLE V.—W = 7·5396 grammes. Mean Density = 0·08912. Mean Pressure = 46·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	ω.
16·20	100·05	536·5	83·85	0·2416
15·00	100·04	536·5	85·04	0·2445
15·77	99·95	536·5	84·18	0·2417
15·21	99·42	536·9	84·21	0·2422
15·54	99·86	536·6	84·32	0·2425

Correction for spheres = − 0·02047.
Other corrections = − 0·00059 ; ϖ = 0·22144.

Deduced specific heat = 0·18691.

TABLE VI.—W = 6·4989 grammes. Mean Density = 0·07710. Mean Pressure = 40·5 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	ω.
15·42	99·18	537·1	83·76	0·2071
16·21	99·29	537·0	83·08	0·2085
15·30	99·73	536·7	84·43	0·2080
15·76	99·76	536·7	84·00	0·2078
14·90	99·95	536·5	85·05	0·2097
15·85	99·92	536·5	84·07	0·2075
15·57	99·63	536·7	84·06	0·2081

Correction for spheres = −0·02042.
Other corrections = −0·00051. ϖ = 0·18717.

Deduced specific heat = 0·18388.

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TABLE VII.—W = 5·3255 grammes. Mean Density = 0·06349.
Mean Pressure = 35·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
14·92	99·99	536·5	85·07	0·1719
15·81	100·02	536·5	84·21	0·1723
14·98	100·09	536·4	85·11	0·1728
16·14	100·00	536·5	83·86	0·1701
14·50	100·05	536·5	85·55	0·1750
15·27	100·03	536·5	84·76	0·17242

Correction for spheres = − 0·02056.
Other corrections = − 0·00047. ϖ = 0·15139.

Deduced specific heat = 0·17994.

TABLE VIII.—W = 4·1450 grammes. Mean Density = 0·04980.
Mean Pressure = 28·5 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
15·52	100·00	536·5	84·48	0·1367
15·02	100·04	536·5	85·02	0·1360
16·17	100·04	536·5	83·87	0·1345
15·38	100·07	536·5	84·69	0·1355
16·68	100·07	536·5	83·98	0·1349
15·70	100·11	536·4	84·41	0·1355
15·74	100·05	536·5	84·31	0·13551

Correction for spheres = − 0·02053.
Other corrections = − 0·00038. ϖ = 0·11460.

Deduced specific heat = 0·17593.

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Table IX.—W = 3·0962 grammes. Mean Density = 0·0377. Mean Pressure = 21·6 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
17·17	100·12	536·4	82·95	0·1010
16·00	100·15	536·4	84·15	0·10405
17·32	100·11	536·4	82·79	0·1031
15·90	100·09	536·4	84·19	0·1038
17·01	100·04	536·5	83·03	0·1032
15·90	99·93	536·5	84·03	0·10395
15·70	100·25	536·5	84·55	0·1046
16·43	100·10	536·4	83·67	0·10338

Correction for spheres = — 0·02031.
Other corrections = — 0·00030. ϖ = 0·08277.

Deduced specific heat = 0·17138.

The unsteadiness of the results with 3 grammes of CO_2 caused me to carry the reduction of mass no further. A test of purity applied to the remaining gas afforded a result the same as the former test. Both samples were from the one bottle.

The following experiments were now made on the empty vessel :

Table X.—Comparison of the Empty Spheres.

t_1.	t_2.	$t_2 - t_1$.	w_1.
16·34	99·95	83·61	—0·0201
17·29	99·93	82·64	—0·0202
17·30	100·01	82·71	—0·0209
15·60	99·94	84·34	—0·0202
15·11	100·07	84·96	—0·0201
		83·65	—0·0203

These apply to the results in Tables III.–IX., as well as to the results in Tables XI. and XII. Some (additive) alterations had been made to the platinum catchwater. To these I in part ascribe the discrepancies between Tables II. and X. It is probable, too, that a small quantity of the phosphoric anhydride had been carried into the sphere in filling it with gas for the experiments of Tables III.–IX., for it was observable that the mass introduced, according to the weighings made upon its insertion, appeared to be 9·6513, while the addition of all the quantities liberated, gave 9·6339 grammes. As there was certainly no leakage at any time, the weights obtained upon release of gas were adopted as true weights.

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After this, all experiments were carried out in the new form of calorimeter described in Part III. To connect its results with those obtained in the old apparatus, the next set (Table XI.) were made upon gas taken from the same bottle used for the foregoing experiments. There is satisfactory agreement with the results of Table VII.

Table XI.—W = 5·1585 grammes. Mean Density = 0·0604.
Mean Pressure = 34·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
14·80	100·08	536·5	85·28	0·1682
15·71	100·07	536·5	84·36	0·1667
14·85	100·14	536·4	85·29	0·16805
15·12	100·10	536·5	84·98	0·16765

Correction for spheres = − 0·02062.
Other corrections = − 0·00045. ϖ = 0·14658.

Deduced specific heat = 0·17940.

The next set (Table XII.) were carried out on gas prepared from bicarbonate of soda by pure sulphuric acid and pumped into the sphere through drying tubes (as described in Part I.). The impurity in this gas was found to be 1 part (of air ?) in 1105 by volume.

Table XII.—W = 4·6290 grammes. Mean Density = 0·0554.
Mean Pressure = 30·0 Atmospheres.

t_1.	t_2.	λ.	$t_2 - t_1$.	w.
14·95	100·05	536·5	85·10	0·1528
15·00	99·67	536·7	84·67	0·15145
15·73	99·70	536·7	83·97	0·1489
14·81	99·93	536·5	85·12	0·1513
15·67	99·89	536·6	84·22	0·1502
15·10	99·84	536·6	84·74	0·1512
15·02	99·62	536·8	84·60	0·1495
15·18	99·81	536·6	84·63	0·15076

Correction for spheres = − 0·02054.
Other corrections = − 0·00042. ϖ = 0·12980.

Deduced specific heat = 0·17780.

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The next table contains the foregoing results collected. I have added, for convenience of reference, the experiments on carbon dioxide contained in Part I. (*loc. cit.*). The mean density is designated ρ.

TABLE XIII.—Experiments on Carbon Dioxide. Low Pressure.

No.	W.	t_1.	t_2.	ρ.	Mean pressure.	Sp. heat.
I.	10·542	16·90	99·98	0·1238	59·0	0·1963
III.	9·634	16·10	99·40	0·1132	55·0	0·1930
IV.	8·625	15·98	99·71	0·1016	51·0	0.1895
V.	7·539	15·54	99·86	0·0891	46·0	0·1869
VI.	6·499	15·57	99·63	0·0771	40·5	0·1839
VII.	5·325	15·27	100·03	0·0635	35·0	0·1799
VIII.	4·145	15·74	100·05	0·0498	28·5	0·1759
IX.	3·096	16·43	100·10	0·0377	21·6	0·1714
XI.	5·158	15·12	100·10	0·0604	34·0	0·1794
XII.	4·629	15·18	99·81	0·0554	30·0	0·1778
Included in Part I.						
I.	2·928	9·26	99·97	0·01995	12·2	0·1705
II.	2·902	10·25	99·33	0·01978	12·1	0·1692
III.	1·562	10·46	99·64	0·01153	7·2	0·1684
IV.	5·552	10·26	99·76	0·03653	20·90	0·1730
V.	5·757	10·83	100·01	0·03780	21·66	0·1739
VI.	4·265	10·82	100·16	0·02850	16·87	0·1714

The results collected in Table XIII. are not obtained without applying to the experimental results the corrections described in Part I., pp. 85, *et seq.* The following data apply :—

Internal volume of active vessel = 101·737 cub. centims. at 16°·0 C.

Elastic yielding = 0·0891 cub. centim. for a pressure of 44·5 atmospheres.

The next table (XIV.) contains the principal data used in the calculations of corrections.

TABLE XIV.—Data for Calculation of Corrections.

Table.	V_{t_1}.	P_1.	$V_{t_1P_1}$.	P_2.	$V_{t_1P_2}$.	α.	Cor. I.	Cor. II.	Cor. VII.
						0·00	−0·000	−0·0000	+0·000
I.	86·127	44·5	86·216	71·0	86·257	532	96	9	18
III.	86·125	42·0	86·208	66·0	86·245	550	90	negligible	18
IV.	86·124	39·5	86·198	60·0	86·234	576	77	,,	15
V.	86·122	36·0	86·189	54·0	86·220	543	72	,,	13
VI.	86·123	32·6	86·182	47·0	86·208	540	62	,,	11
VII.	86·121	29·4	86·174	39·0	86·191	450	56	,,	09
VIII.	86·123	22·9	86·164	31·2	86·179	428	44	,,	06
IX.	86·126	17·9	86·158	23·7	86·169	387	35	,,	05
XI.	86·121	27·3	86·170	38·8	86·191	494	53	,,	08
XII.	86·121	25·2	86·166	34·9	86·184	456	49	,,	07

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Referring to Part I., for a general account of the corrections to be applied to these experiments, it is only necessary to recall here sufficient to explain the contents of the last table. In calculating the correction due to the effect of the thermal increase of volume of the vessel upon the contained gas several quantities have first to be deduced. The equation for the work done by the gas is

$$\epsilon = \{P_1 V_1 \beta (t_2 - t_1)\} \{1 + (\alpha - \beta) \tfrac{1}{2} (t_2 - t_1)\}.$$

The amount of this correction, expressed as a weight of steam precipitated upon the vessel, is to be deducted from the observed weight of precipitation. This subtractive quantity is given in the column headed Cor. I. of the table, the corrections being numbered in accordance with Part I. It is based upon the numbers contained in the previous column. The second column contains the initial volume of the sphere corrected for temperature only, on a coefficient of thermal expansion (β) of 0·00005. The third column contains an approximate estimate of the pressure P_1, in atmospheres, due to the weight, W, of gas in the vessel at the initial temperature, t_1. In the fourth column the effect of the pressure upon the volume of the vessel is recorded, basing calculations upon the elastic yielding of the vessel experimentally found, as above. An estimate of the pressure, P_2, at the steam temperature is given in the fifth column, and the distending effect of this in the sixth. The manner of estimating the pressures is described later. The quantitiy, α, is given in the seventh column. It is calculated on the equation

$$\alpha = \frac{P_2 - P_1}{(t_2 - t_1) P_1}.$$

By use of the second and sixth columns, and the third reduced to dynes, Cor. I. is calculated.

Correction II. deals with the elastic distension of the vessel and the effect of this in producing thermal effects on the contained gas. For this, the work

$$\eta = P_1 V_1 \log \epsilon \frac{V_2}{V_1},$$

or, in grammes of water,

$$\varpi_1 = \frac{(P_1 V_1) \{(\log V_2 - \log V_1)(2{\cdot}30)\}}{22500},$$

the second, third, and seventh columns being used. Except in the case of the first experiment, however, this turns out to be a negligible correction.

The column headed correction VII. contains the additive Correction obtained upon reducing the weight of precipitated water to vacuo. The other corrections treated of in Part I. are found to be negligible for these experiments, excepting, of course, that arising from the unequal thermal capacity of the two spheres. Thus, the correction for buoyancy due to distension of the sphere, while in the steam, numbered 4 in Part I., affords but 0·02 of a milligramme in the most extreme case, and the others

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(3 and 5 of Part I.) are completely inappreciable. The final correction therefore to be applied to each experiment is got by subtraction of the minus corrections I. and II., and addition of the plus correction VII. Each of the tables of experiments contains this amount at the foot, it being understood that the mean of each series of experiments is treated in all cases as the experiment to be corrected.

I have not tabulated the figures used to derive the density of the gas, as they can be verified comparatively easily from the table of corrections already given. Thus the mean density ρ of table XIII. is the quotient obtained when the *total* weight of gas in the sphere is divided by the mean volume of the sphere. The first quantity is got by adding to W, recorded at the head of each table of experiments, the weight of a volume of carbon dioxide equal to the initial volume of the sphere and at atmospheric pressure. For evidently this last quantity of gas, while it does not enter into the estimate of the mass producing the observed calorimetric effect—as it remains in the sphere during the comparison of the inactive vessels—yet must be considered in estimating the actual density of the gas. For the foregoing series, I. to X., a mass = 0·1587 gramme of gas is added in each case to W; calculated on a volume of 86·12 cub. centims., a temperature of 16°·7 C., and a pressure of 760 millims., the approximate volume, temperature, and pressure obtaining.

The mean volume is obtained from the table for corrections (XIV.) by adding to the volume at t_1 and P_1 the increase of volume due to the rise of pressure $\frac{1}{2}(P_2 - P_1)$, and also the increase of volume due to the rise of temperature $\frac{1}{2}(t_2 - t_1)$.

Finally, the mean pressure obtaining during experiment is evidently that exerted by the total mass of gas confined in the volume obtaining at mean temperature augmented by the elastic distension due to the mean pressure sought. As, for calculation of errors, it is necessary to estimate the initial and final pressures due to W (not to the total mass), it is convenient and sufficiently accurate to add to the mean pressure due to W, the pressure due to the mass added, as above, in ascertaining the total mass. We may calculate this pressure on ANDREWS' coefficient 0·0037 for change of pressure at constant volume between 20° and 100°. The pressure so estimated is found to be 1·15 atmosphere. I may observe, however, that I departed only so far from accuracy as to add the one atmosphere, as the degree of accuracy attained in estimating P_1 and P_2, and the mean pressure due to W, did not warrant addition of small quantities.

The higher pressures were ascertained from AMAGAT's recently published tables of the isothermals of carbon dioxide ('Annales de Chimie et de Physique,' 6th series, vol. 29). A chart of densities (as abscissæ) and pressures (as ordinates) was constructed. The mass affording the V in AMAGAT's tables, is that of unit volume of carbon dioxide at 0° and 760 *i.e.*, 0·0019767 gramme. Hence

$$\delta = \frac{P \times 0\cdot0019767}{(PV)}.$$

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This is convenient for use of the slide rule. On this chart, vertical lines were drawn at the particular densities cutting the isothermals at points which afforded the pressures corresponding to the several isothermals. Unfortunately, AMAGAT's results do not descend to absolute densities below 0·08. For densities below this, I had to call in the few estimations of ANDREWS'. From these, curves were also plotted, but, conveniently, of a different character. ANDREWS, in fact, gives pressures in atmospheres and fractional decrease of volume (*i.e.*, the fraction V_1/V_2) at the temperatures 6°·5, 64°, and 100° ('Proc. Roy. Soc.,' 24, p. 458). Plotting these against each other we obtain isothermals which may be availed of by calculating the diminution of volume of the gas in the sphere at the temperatures of the isothermals as above. This is readily done, as the volume of the sphere (V_2) and the volume (V_1) of the mass W at one atmosphere and at the above temperatures, may be calculated. These known, and the quotient of V_1/V_2 marked upon the isothermals, the points so formed may be joined by lines crossing the isothermals diagonally, from which pressures, at any intermediate temperatures, may be ascertained. The mean pressures and the values of P_1 and P_2 were taken separately from these charts. At the lowest densities, the estimation of pressure is not very satisfactory. All the data necessary to amend the result at any time, when more connected results are available, are however contained in the tables.

Upon the completion of the foregoing experiments, as the limit of stress to which the vessel might be subjected had not been reached, a fresh series was begun extending to higher densities. The sphere was tested with 18·7 grammes of the gas at 100° for 15 minutes. The sphere, as already mentioned, further increased in volume. The experiments then carried out are contained in Table XV.

TABLE XV.—Experiments at High Densities.

No.	W.	t_1.	t_2.	λ.	ω.	*a*.	*b*.	C_v.	ρ.	Mean P.
						— 0·0	— 0·00			
1	18·7647	12·38	99·98	536·5	1·0120	257	091	0·**3223**	0·2096	81·5
2	18·7647	12·33	100·09	536 5	1·0175	257	091			
3	18·7647	13·39	100·08	536·5	0·9583	255	097	0·**3074**	0·2095	82·0
4	16·8398	12·50	100·17	536·4	0·8347	257	090	0·**2917**	0·1882	76·7
5	16·8398	12·86	100·23	536·3	0·8213	257	090			
6	16·8398	14·60	100·18	536·4	0·6533	251	109	0·**2334**	0·1882	77·0
7	15·7502	15·57	100·25	536·3	0·6045	248	134	0·**2326**	0·1762	75·0
8	15·7502	12·56	100·49	536·2	0·7285	258	118	0·**2717**	0·1763	74·0
9	14·0313	14·15	100·53	536·1	0·5182	253	128	0·**2175**	0·1572	69·0
10	14·0313	12·14	100·61	536·1	0·5771	260	118	0·**2376**	0·1573	68·5
11	12·8617	15·09	100·60	536·1	0·4416	251	097	0·2025	0·1443	65·5
12	12·8617	12·52	100·64	536·1	0·4561	259	115	0 2030	0·1444	65·0
13	11·7664	14·44	100·62	536·1	0·4031	253	099	0·1992	0·1323	61·5
14	11·7664	12·67	100·60	536·1	0·4119	260	099	0·1994	0·1322	61·0
15	10·4660	12·47	100·53	536·1	0·3624	260	091	0·1948	0·1178	56·5
16	10·4660	12·91	100·47	536·2	0·3594	260	091			
17	10·4660	15·49	100·44	536·2	0·3478	249	090	0·1942	0·1177	57·0

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Looking at the three first experiments upon 18·7647 grammes of gas, it is seen that the first two, having nearly the same range, afford a like precipitation (ω) and the deduced specific heat is 0·322; but the third experiment, which is over a range commencing at a temperature (t_1) only one degree higher than the initial temperature of Nos. 1 and 2, affords a specific heat 0·307. This difference of 5 per cent. reveals the existence of a large thermal effect dependent upon t_1. In short, liquid carbon dioxide is present at the initial temperature. Looking down the table it is observable that so far as Experiment 10, similar wide variations of specific heat with small change of initial temperature occur. The remainder are sensibly free from this effect due to latent heat. Thus, compare 11 with 12, and 13 with 14. All these last, from 11 downwards, plot upon the prolongation of previous observation; the others, as might be expected, lie upon a line rapidly bending upwards, away from the axis of density, and are not contained in the chart.

The correction contained in column "*a*" is that due to the different thermal capacities of the vessels. It is derived from experiments given in Table XVI.

TABLE XVI.—Comparison of the Empty Spheres.

t_1.	t_2.	$t_2 - t_1$.	w.
15·30	100·65	85·35	− 0·0247
12·89	100·42	87·53	− 0·0256
12·79	99·87	87·08	− 0·0258
		86·65	− 0·0254

It will be observed that the correction is larger than formerly. This is in part accounted for by the increased volume of the active sphere. The change of medium during experiment produces an effect = V × 0·00062 (the difference of density of saturated steam and air at 100°), and in this way the increased volume of nearly 4 cub. centims. causes an effect upon the balance of 0·0025 gramme. The outstanding increase in ω is probably ascribable to lodgement of P_2O_5 in the vessel, or even possibly to some chemical action between the CO_2 and the copper. From the mode of estimating W, upon liberation of the gas, this produces no error.

In column "*b*," Table XV., is contained the result of all the other corrections calculated as in the previous experiments. The internal volume of the sphere is now 89·984 cub. centims. at 13°·2 C. The elastic distension is taken as before. From these data the numbers in the next table are calculated.

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TABLE XVII.—Calculation of Corrections.

No.	V_{t_1}.	P_1.	$V_{t_1 P_1}$.	P_2.	$V_{t_1 P_2}$.	α.	Cor. I.	Cor. II.	Cor. III.
						0·0	– 0·00	– 0·000	+ 0·000
1, 2	89·980	46·7	90·060	107·0	90·179	149	101	15	59
3	89·985	48·0	90·074	107·0	90·184	143	103	15	55
4, 5	89·982	47·1	90·069	98·5	90·167	127	100	15	48
6	89·993	49·5	90·081	98·5	90·175	120	104	15	37
7	89·993	50·8	90·086	94·0	90·167	103	122	15	30
8	89·982	46·9	90·069	94·0	90·156	114	119	15	40
9	89·988	48·9	90·078	86·0	90·147	088	121	15	30
10	89·980	46·4	90·066	86·0	90·139	096	118	15	30
11	89·992	48·0	90·082	80·0	90·141	076	102	15	20
12	89·982	46·5	90·069	80·0	90·131	081	108	15	20
13	89·900	45·5	89·991	74·5	90·039	061	104	15	20
14	89·982	45·0	90·071	74·5	90·121	063	104	15	20
15, 16	89·982	42·0	90·068	68·0	90·111	062	096	15	20
17	89·993	43·0	90·077	68·0	90·122	061	095	15	20

The values of P_2 as well as the mean pressures in atmospheres are directly scaled from the plot of AMAGAT'S experiments, in which, as explained, pressure is plotted against density, and have little uncertainty about them. In the calculation of the mean pressures, as given in Table XV., one atmosphere is added. The values of P_1 (Experiments 1 to 10) are obtained from AMAGAT'S table of pressures at saturation of carbon dioxide (*loc. cit.*, p. 70). From this, too, we derive the following table, giving the masses of liquid and gas present at the initial temperatures of the experiments 1 to 10, and the approximate temperature at which the liquid was entirely evaporated in each case.

TABLE XVIII.

No.	Grams. of liquid present at t_1.	Grams. of gas at t_1.	All gas.
			°
1 and 2	7·104	11·660	30
3	6·571	12·194	30
4 and 5	4·523	12·317	20
4	4·670	12·170	20
6	3·648	13·192	20
7	1·686	14·074	18
8	3·358	12·392	18
9	0·551	13·480	15
10	1·510	12·520	15

The chart on the next page showing the plotting of the experiments contained in this paper, and those on carbon dioxide contained in Part I., reveals that the specific heat plotted against density follows a slightly curved line, convex towards density. The plotting could only be carried so far as the density 0·150, owing to the presence

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of liquid, at the initial temperature, above this density. Nor had I sufficient data to calculate out the latent heat effect, &c., due to presence of liquid at higher densities.

The former expression for the dependence of specific heat on density, ρ, was

$$C\gamma = 0{\cdot}16577 + 0{\cdot}2064\rho.$$

A more accurate formula embracing all the experiments up to $\rho = 0{\cdot}150$ may now be obtained :—

$$C\gamma = 0{\cdot}1650 + 0{\cdot}2125\rho + 0{\cdot}340\rho^2.$$

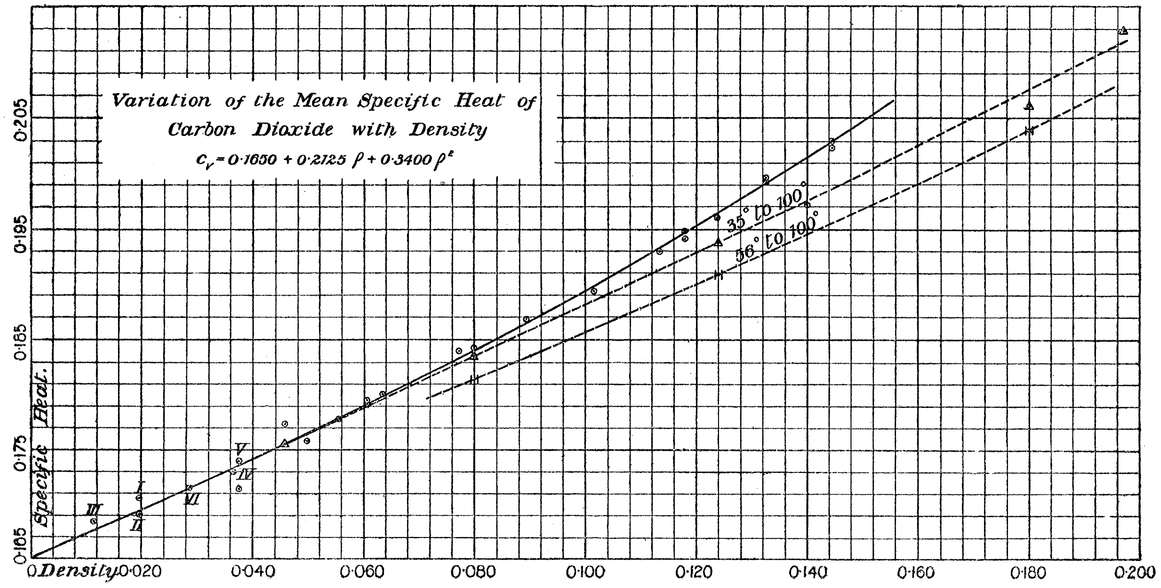
This accurately interprets the line carrying the mean results of the observations. At zero density, the specific heat at constant volume is thus 0·1650.

The expression must only be considered as applying over the interval 12° to 100° C., and not beyond the density 0·150. As observed, the presence of liquid renders it inaccurate at higher densities. It is needful to define the initial temperature, seeing that the results of the observations recorded in Part III. show that at densities lying even much below 0·150 the rate of variation of the specific heat with change of density is dependent upon the range of temperature obtaining.

It is convenient to indicate these results upon the plate. Accordingly, a dotted line below the full curve conveys the specific heat over the range 35° to 100°, and one below this the specific heat between 56° and 100°. A third range of temperature is dealt with in Part III., but its data are insufficient for plotting upon the plate; the results for this range, 78° to 100°, would appear to lie still lower.

It is to be observed that the curvature almost dies out for the higher ranges of temperature. In fact, the gas behaves then more nearly as a perfect gas. Thus, from 35° to 100°, the specific heat is given, closely, by

$$C\gamma = 0{\cdot}1650 + 0{\cdot}2300\rho.$$



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