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

On the Ratio of the Specific Heats of Some Compound Gases

J. W. Capstick

Phil. Trans. R. Soc. Lond. A 1895 **186**, 567-592
doi: 10.1098/rsta.1895.0015

XV. *On the Ratio of the Specific Heats of Some Compound Gases.*

By J. W. CAPSTICK, *M.A., D.Sc., Fellow of Trinity College, Cambridge.*

Communicated by Professor J. J. THOMSON, *F.R.S.*

Received January 25,—Read February 14, 1895.

§ 1. *Introduction.*

THE experiments to be described in the present paper are a continuation of those of which I gave an account in the 'Phil. Trans.,' vol. 185, p. 1.

It is shown there, from experiments on methane, ethane, and propane, and their derivatives, that the monohalogen derivatives of any one paraffin have in the gaseous state the same ratio of the specific heats, and that this ratio is the same as that of the hydrocarbon itself in two of the three series. Methane proved to be an exception, having a higher ratio than its derivatives.

It seemed to be a matter of some interest to find whether the same was true of unsaturated hydrocarbons and their monohalogen derivatives, and also to find the effect of introducing more than one halogen atom into the molecule. The aim of most of the experiments described below was to get information on these two points.

It is not necessary to give a detailed account of the apparatus and method of procedure, since they were the same as those described in the paper mentioned above. KUNDT's dust-figure apparatus was used for finding the ratio of the wave-lengths of sound of a given pitch in air and in the gas under investigation, and the ratio of the specific heats was calculated by means of the formula

$$\gamma = 1{\cdot}408 \times \rho \times \left(\frac{l}{l'}\right)^2 \left(1 + \frac{1}{p}\frac{d}{dv}pv\right);$$

where ρ is the specific gravity of the gas referred to air, l and l' the lengths of the dust-figures in the gas and in air respectively, and the last factor is the correction for the deviation of the gas from BOYLE's Law.

The vapour density of the gas was found experimentally at several different pressures, and from the curve plotted from the results ρ and the correction factor were determined in the way previously described.

Some of the substances used in this investigation are very difficult to purify, hence it is a matter of importance that when γ is determined in the way described, the

24.9.95

result is only very slightly affected by the presence of a little impurity. Impurities make themselves felt mainly by their modifying the density of the gas, and error from this source is avoided by the vapour density determination having been made in nearly every case on the same samples of the material as were used in the velocity of sound experiments. Hence impurity only has an effect in so far as the γ of the foreign substance is not the same as that of the gas under investigation. An estimate of the amount of this error can be got by an application of equation (5) of my former paper. If, for instance, the methylene chloride contained 1 per cent. of chloroform, the error in γ would be less than one part in a thousand.

Except where the contrary is stated, the materials were obtained from KAHLBAUM and were dried and fractionated before being used. The following table of the observed range of boiling-points of definite quantities of the liquids as actually employed in the experiments will give some indication of the degree of purity obtained.

TABLE I.

Name.	Quantity.	B. P. (uncorrected).
Methylene chloride	50 c.c.	43°·5 to 44°·3
Chloroform	300	60·8 ,, 61·2
Carbon tetrachloride	50	76·8 ,, 76·9
Ethylene chloride	60	83·9 ,, 84·1
Ethylidene chloride	40	59 ,, 60·1
Allyl chloride	110	45 ,, 46·5
Allyl bromide	70	69 ,, 71
Ethyl formate	200	56
Methyl acetate	400	56 to 57·5
Carbon bisulphide	250	46·8 ,, 47

As regards the degree of accuracy attainable in the measurements I must again refer to my former paper. On p. 11 is given a typical set of measurements of the dust figures, and on p. 27 a series of experiments on ethyl chloride that afford a test of the accuracy of the vapour density determinations.

The experiments on carbon dioxide (Table XXII., below) show further, that whilst the work was in progress no change took place in the apparatus that affected the results. The first three experiments on carbon dioxide were made when the apparatus was first set up ; the last three were made two years later, after it had been repeatedly dismantled for cleaning, and repairs and most of the original tubes had been replaced by others. The two sets of three give almost identical results.

Many of the gases used in the experiments have low saturation pressures at the atmospheric temperature—a fact which tends to increase the experimental error, for small errors in reading the height of the mercury column in the vapour density apparatus have a more serious effect when the total pressure to be measured is small, and in addition to this, the small range of pressure available makes it difficult to draw the isothermal curve accurately. Hence the vapour-density determinations in some cases give a rather irregular curve, but when the divergences are so great as to leave much doubt how the curve should be drawn, I have made a separate determination of the relative densities in the way described under ethyl chloride in my former paper.

The column headed β in the tables below, gives the ratio of the rates of increase with rise of temperature of the internal energy of the molecule and its kinetic energy of translation.

The usual equation connecting β and γ, viz.,

$$\beta + 1 = \frac{2}{3(\gamma - 1)},$$

is deduced on the assumption that the gas is perfect, for it neglects the change of potential energy due to separation of the molecules on expansion, and assumes that pv is proportional to t.

For air and a few other gases this is a matter of no consequence, but when we come to vapours not far removed from saturation, it is necessary to use a better formula, or at least to find whether the error made by using the old one is serious compared with the experimental error.

Since, to a first approximation, pv is equal to Rt, we may write the characteristic equation in the form

$$pv = \mathrm{R}t + f(p, v, t) \quad \ldots \ldots \ldots \quad (1),$$

where f is so small that its square and the squares of its differential coefficients can be neglected.

Now we know from thermodynamics that

$$\mathrm{C}_p - \mathrm{C}_v = t\,(dp/dt)_v\,(dv/dt)_p \quad \ldots \ldots \ldots \quad (2),$$

and from equation (1) we get by differentiating at constant volume and pressure respectively

$$\left(\frac{dp}{dt}\right)_v = \frac{\mathrm{R} + df/dt}{v - df/dp}$$

$$\left(\frac{dv}{dt}\right)_p = \frac{\mathrm{R} + df/dt}{p - df/dv}$$

Hence

$$\mathrm{C}_p - \mathrm{C}_v = \frac{t\,(\mathrm{R} + df/dt)^2}{(p - df/dv)\,(v - df/dp)}$$

$$= \frac{\mathrm{R}^2 t}{pv}\left(1 + \frac{1}{p}\frac{df}{dv} + \frac{1}{v}\frac{df}{dp} + \frac{2}{\mathrm{R}}\frac{df}{dt}\right),$$

neglecting squares of the differential coefficients, or, since

$$Rt = pv - f,$$

therefore

$$C_p - C_v = R\left(1 - \frac{f}{pv}\right)\left(1 + \frac{1}{p}\frac{df}{dv} + \dots\right)$$
$$= R\left(1 + \frac{1}{p}\frac{df}{dv} + \frac{1}{v}\frac{df}{dp} + \frac{2}{R}\frac{df}{dt} - \frac{f}{pv}\right) \quad . \quad . \quad . \quad (3).$$

If $\delta\tau$ is the increase of the kinetic energy of translation of the molecules in unit mass of the gas for a rise of temperature δt, we have

$$C_v\,dt = \delta\tau + \beta\,\delta\tau$$
$$= \tfrac{3}{2}(1 + \beta)\,R\,\delta t,$$

since

$$\tfrac{2}{3}\tau = Rt.$$

Hence

$$R = \tfrac{2}{3}\frac{C_v}{1 + \beta},$$

and dividing out C_v, equation (3) becomes

$$\gamma - 1 = \frac{2}{3(1 + \beta)}\left(1 + \frac{1}{p}\frac{df}{dv} + \frac{1}{v}\frac{df}{dp} + \frac{2}{R}\frac{df}{dt} - \frac{f}{pv}\right) \quad . \quad . \quad . \quad (4).$$

If the form of $f(p, v, t)$ were known we could readily put equation (4) into a form fitted for calculation. Unfortunately we cannot use the characteristic equations proposed by CLAUSIUS, VAN DER WAALS, TAIT, and others, for the constants of these equations are not known except for a few gases.

There is however not much lost by taking an approximate value of the term in brackets, for from the nature of the equation the experimental error in γ is considerably increased in β.

By differentiating the approximate equation

$$\beta + 1 = \tfrac{2}{3}\frac{1}{\gamma - 1}$$

we get

$$\frac{\delta\beta}{\beta}\Big/\frac{\delta\gamma}{\gamma} = -\frac{2\gamma}{(\gamma - 1)(5 - 3\gamma)}.$$

Hence, if

$$\gamma = 1{\cdot}3 \qquad \frac{\delta\beta}{\beta}\Big/\frac{\delta\gamma}{\gamma} = -\ 8$$
$$= 1{\cdot}2 \qquad\qquad = -\ 9$$
$$= 1{\cdot}1 \qquad\qquad = -12$$

Thus, since any error in γ is increased tenfold in β, it is useless to do much more than find roughly the magnitude of the correction, until our experimental methods for determining γ are much improved.

If we take CLAUSIUS' equation

$$p = \frac{\mathrm{RT}}{v - a} - \frac{\mathrm{C}}{\mathrm{T}\,(v + b)^2}$$

as the characteristic equation of a gas, we can, by making certain approximations, express the correction for β in terms of $\frac{1}{p}\frac{d}{dv}(pv)$.

At ordinary temperatures and pressures a and b are negligible compared with v, so that f may be taken to be $-\mathrm{C}/\mathrm{T}v$.

Hence

$$\frac{1}{p}\frac{df}{dv} = \frac{\mathrm{C}}{\mathrm{T}pv^2} = \frac{\mathrm{C}}{\mathrm{RT}^2v}$$

$$\frac{1}{v}\frac{df}{dp} = 0$$

$$\frac{2}{\mathrm{R}}\frac{df}{dt} = \frac{2\mathrm{C}}{\mathrm{RT}^2v}$$

$$-\frac{f}{pv} = \frac{\mathrm{C}}{\mathrm{RT}^2v},$$

therefore

$$\beta + 1 = \frac{2}{3(\gamma - 1)}\left\{1 + \frac{4\mathrm{C}}{\mathrm{RT}^2v}\right\}$$

and

$$\frac{1}{p}\frac{d}{dv}(pv) = \frac{\mathrm{C}}{\mathrm{T}v^2p} = \frac{\mathrm{C}}{\mathrm{RT}^2v}.$$

Hence

$$\beta + 1 = \frac{2}{3(\gamma - 1)}\left\{1 + \frac{4}{p}\frac{d}{dv}(pv)\right\} \quad . \quad . \quad . \quad . \quad . \qquad (5).$$

Equation (5) has been used in calculating β in all the tables that follow.

In my former paper I pointed out (p. 34) that the γ of ethyl chloride and a few other gases appeared to be greater at the higher pressures, and mentioned that the effect might be due merely to the divergence of the gas from BOYLE'S law, and not to any change in the value of β. This appears to be the case, for if β is calculated from the results by means of formula (5), the progressive change disappears. The table below shows this for ethyl chloride, where the change in γ is most marked.

Table II.

p.	γ.	β.
millims. 200	1·180	2·878
205	1·180	2·878
285	1·189	2·751
295	1·180	2·939
400	1·191	2·754
400	1·188	2·814
410	1·184	2·896
560	1·193	2·797
610	1·190	2·858
630	1·192	2·818

The values of β naturally diverge more widely from the mean than do those of γ, but there is no longer any progressive change to be seen, and we may conclude that the ratio of internal to translational energy of a molecule does not depend on the average distance between the molecules.

§ 2. *Methylene Chloride.* (CH_2Cl_2.)

Table III. gives the results of five determinations of the vapour-density of methylene chloride. The first column gives the pressure to the nearest millimetre at which the experiment was made, the second column gives the temperature, and the third gives the specific gravity of the gas referred to air at the same temperature and pressure.

Fig. 1 shows the curve plotted from the results.

Table III.

p.	t.	ρ.
135	19·2	3·081
155	18·6	3·087
160	18·9	3·086
199	18·6	3·094
211	16·7	3·096

Fig. 1.

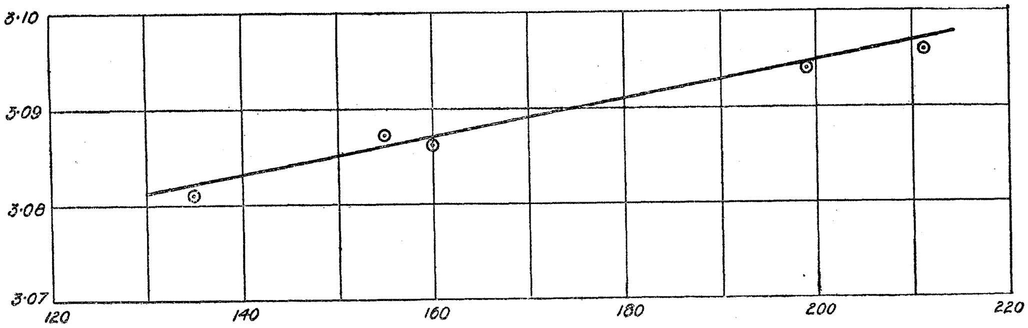

Table IV. gives the final results calculated from three determinations of the velocity of sound in the vapour.

The letters at the heads of the columns have the following meanings :—

p. The pressure of the vapour in the Kundt apparatus when the dust figures were made.

t. The temperature of the vapour.

l. The length of the dust figures in methylene chloride.

l'. " " " " air.

ρ. The specific gravity of the vapour at the pressure at which the experiment was made. This specific gravity was taken from the curve in fig 1.

$1 + \frac{1}{p}\frac{d}{dv}\overline{pv}$. The correction for deviation from Boyle's Law, calculated as described in my former paper.

γ. The ratio of the specific heats, calculated by means of the formula on p. 567.

β. The ratio of the rates of increase of internal and translational energy of the molecule with rise of temperature, calculated by formula (5) on p. 571.

Table IV.

p.	t.	l.	l'.	ρ.	$1+\frac{1}{p}\frac{d}{dv}\overline{pv}$.	γ.	β.
152	16·7	25·57	48·66	3·085	1·011	1·213	2·263
160	19·2	25·76	48·90	3·086	1·011	1·219	2·174
174	19·3	25·81	48·90	3·089	1·011	1·225	2·089
					Mean	1·219	2·175

§ 3. *Chloroform*, $CHCl_3$.

The tables and figures have in this and most of the succeeding cases the same meaning as in the case of methylene chloride.

Table V.

p.	t.	ρ.
97	19·4	4·112
106	21·2	4·114
121	20·6	4·118
138	20·3	4·128

Fig. 2.

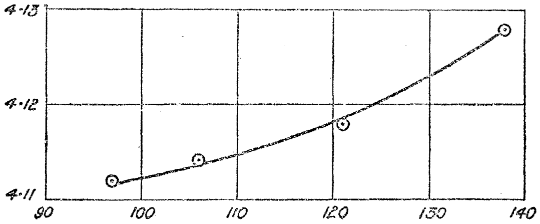

TABLE VI.

p.	t.	l.	l'.	ρ.	$1+\frac{1}{p}\frac{d}{dv}\overline{pv}$.	γ.	β.
109	20	21·73	48·96	4·114	1·008	1·150	3·581
114	21	21·81	49·05	4·116	1·010	1·157	3·414
117	20·2	21·78	48·99	4·117	1·011	1·157	3·427
121	19·8	21·69	48·95	4·118	1·012	1·152	3·593
					Means	1·154	3·506

§ 4. *Carbon Tetrachloride* (CCl_4).

TABLE VII.

p.	t.	ρ.
53	21·7	5·330
64	21·6	5·352
69	19·05	5·350
69	18·8	5·339
77	19·2	5·358
86	20·1	5·368

Fig. 3.

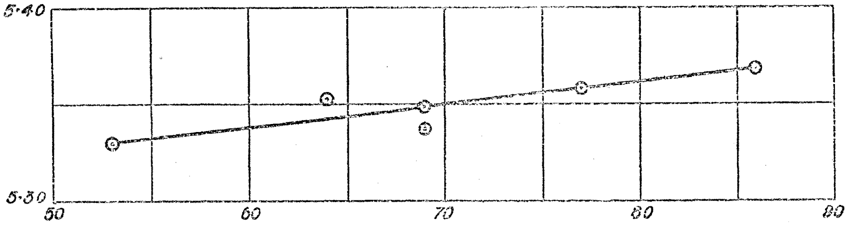

TABLE VIII.

p.	t.	l.	l'.	ρ.	$1+\frac{1}{p}\frac{d}{dv}\overline{pv}$.	γ.	β.
54	20·6	18·86	49·02	5·332	1·012	1·125	4·585
72	20·2	18·85	49·00	5·351	1·014	1·131	4·367
73	20·2	18·87	49·00	5·354	1·014	1·133	4·285
75	20·5	18·83	49·01	5·356	1·014	1·130	4·409
					Mean	1·130	4·411

§ 5. *Ethylidene Chloride* ($CH_3.CH\,Cl_2$).

TABLE IX.

p.	t.	ρ.
121	23·6	3·439
138	25	3·446
146	23·8	3·447
153	24	3·451

Fig. 4.

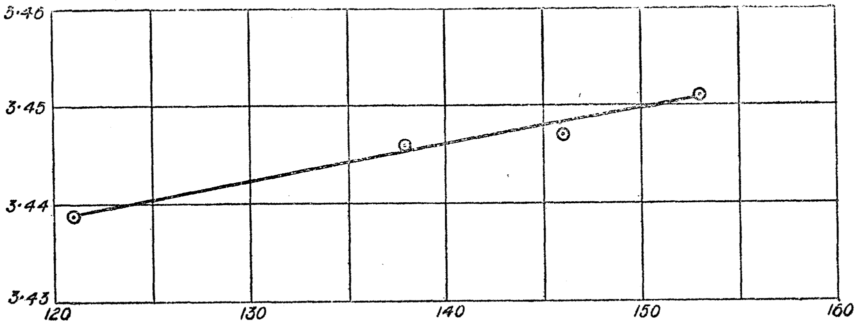

TABLE X.

p.	t.	l.	l'.	ρ.	$1+\frac{1}{p}\frac{d}{dv}\overline{pv}$.	γ.	β.
125	21	23·50	49·03	3·440	1·013	1·127	4·518
132	24	23·74	49·36	3·443	1·014	1·137	4·133
138	23·9	23·73	49·34	3·445	1·015	1·139	4·079
					Mean	1·134	4·243

§ 6. *Ethylene Chloride* ($CH_2Cl.CH_2Cl$).

Ethylene Chloride boils at 85°, and its vapour-pressure at ordinary temperature is so low, that small errors in reading the height of the mercury columns, or, in weighing the liquid, have too great an effect to allow a reliable curve to be drawn from the vapour-density determinations. Consequently these determinations were all made near the same pressure, and the mean of the results was used in the final calculations.

The values found were as follows :—

TABLE XI.

p.	t.	ρ.
42·9	23	3·460
46·1	24	3·442
46·1	23·8	3·437
45·7	24·4	3·448
43·8	22·8	3·443

To find the value of the correction factor a determination of the relative densities at three pressures was made with the apparatus described under Ethyl Chloride in my former paper. The experiment was made at 24°, with the result shown in Table XII.

TABLE XII.

v.	p.	pv.
122·00	37·40	4566
91·17	49·83	4543
66·57	67·88	4519

This gives 1·017 as the value of the correction factor at 45 millims.

Finally, Table XIII. gives the details of the velocity of sound determinations.

TABLE XIII.

p.	t.	l.	l'.	ρ.	$1+\frac{1}{p}\frac{d}{dv}pv$.	γ.	β.
44	19·4	23·56	48·92	3·446	1·017	1·144	3·938
42	18·8	23·46	48·90	..	..	1·135	4·267
48	19·4	23·44	48·92	..	..	1·133	4·346
					Mean .	1·137	4·184

§ 7. *Ethylene* (C_2H_4).

For the material I was indebted to the kindness of Professor Dewar, who gave me a cylinder of compressed ethylene. As the critical temperature of ethylene is near the ordinary atmospheric temperature, the bottle was placed in a freezing mixture to ensure the contents being liquefied, and so to keep back by fractional distillation any ether and water that had escaped the preliminary washing and drying of the gas.

Amagat's experiments on the compressibility of ethylene enable us to calculate the correction due to deviation from Boyle's Law. Since, however, the lowest pressure used by Amagat was 30 atmospheres, the correction term must be put in a slightly different form. Using Van der Waals' equation

$$(p + a/v^2)(v - b) = Rt$$

to express the relation between p, v, and t, it is easily shown that the correction term takes the form $1 + a/pv^2 - b/v$.

Baynes has calculated Van der Waals' constants from Amagat's observations, and finds ('Nature,' vol. 22, p. 186) $a = \cdot 00786$, $b = \cdot 0024$. Hence since in my experiments $p = 1$ and $v = 288/273$, we get the correction 1·007.

Two determinations of the velocity of sound at atmospheric pressure gave the following results, the theoretical value of the density of the gas being used in the calculation of γ.

Table XIV.

t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d}{dv}pv$.	γ.	β.
15·4	46·32	48·51	·9675	1·007	1·251	
15	46·32	48·54	..	..	1·249	
				Mean . . .	1·250	1·740

§ 8. *Vinyl Bromide* (C_2H_3Br).

The material was made by gently warming ethylene dibromide with alcoholic potash. The issuing gas was condensed, fractionated, allowed to stand over calcium chloride, and again fractionated.

Four weighed tubes to contain the liquid for vapour-density determinations were filled in a freezing mixture, but on coming to the temperature of the room two burst, so that only two were left for use. These gave the following results :—

TABLE XV.

p.	t.	ρ.
311	15·2	3·677
436	15	3·700

Since two observations are not sufficient to give the curve, a set of relative density determinations was made in the usual way. The results are shown in Table XIV.

TABLE XVI.

p.	v.	pv.
155·35	12·415	1928
220·6	8·68	1915
250·3	7·627	1914
305·35	6·224	1901
503	3·721	1872

The reciprocals of the numbers in the third column are proportional to the specific gravity of the vapour. These reciprocals with the scale suitably altered so as to coincide as nearly as possible with the values in Table XV. are marked by circles on the curve of fig. 5. The two values of the absolute density are marked by crosses.

The curve was employed in the usual way for finding the numbers in the fifth and sixth columns of Table XVII.

Fig. 5.

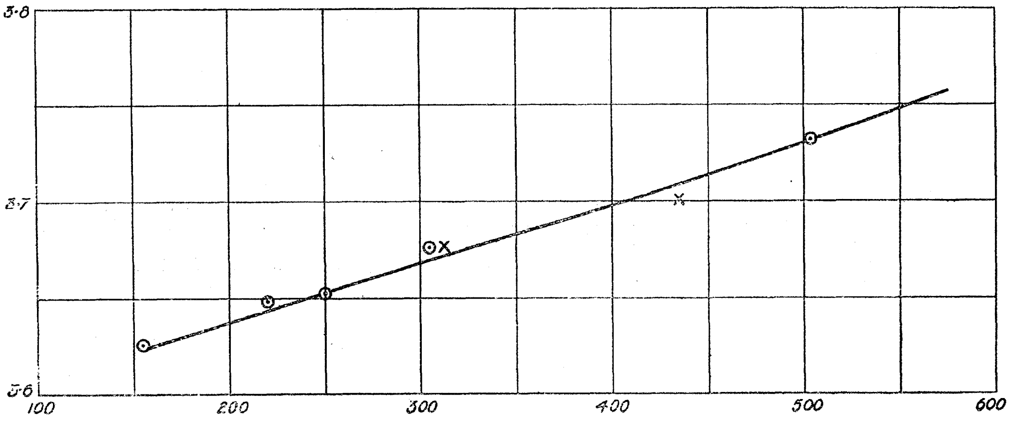

Table XVII.

p.	t.	l.	l'.	ρ.	$1+\frac{1}{p}\frac{d}{dv}\overline{pv}$.	γ.	β.
380	15	22·98	48·53	3·690	1·026	1·195	2·770
430	15·6	22·97	48·63	3·705	1·026	1·193	2·808
560	15·2	22·91	48·54	3·749	1·027	1·207	2·566
					Mean .	1·198	2·715

§ 9. *Allyl Chloride* (C_3H_5Cl).

Table XVIII.

p.	t.	ρ.
96	14·2	2·655
116	13·2	2·660
128	12·8	2·659
152	12·6	2·664
184	15·0	2·667

Fig. 6.

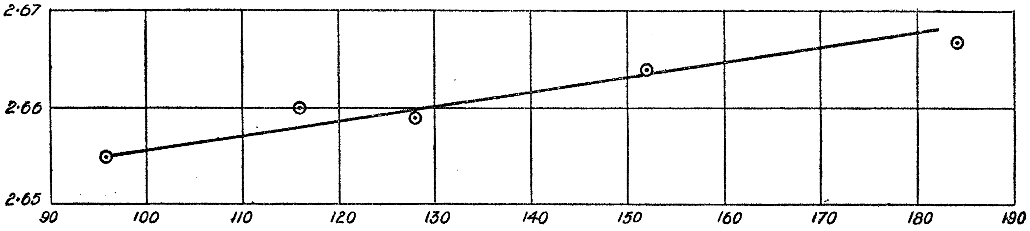

Table XIX.

p.	t.	l.	l'.	ρ.	$1+\frac{1}{p}\frac{d}{dv}\overline{pv}$.	γ.	β.
115	13·5	26·58	48·42	2·658	1·006	1·134	4·090
142	13·2	26·56	48·40	2·662	1·008	1·137	4·016
147	13·6	26·53	48·43	2·663	1·008	1·134	4·128
156	14·7	26·65	48·52	2·665	1·009	1·142	3·859
					Mean . .	1·137	4·023

§ 10. *Allyl Bromide* (C_3H_5Br).

TABLE XX.

p.	t.	ρ.
52	13·4	4·174
74	14·9	4·187
70	16·4	4·184
68	16·2	4·188

Fig. 7.

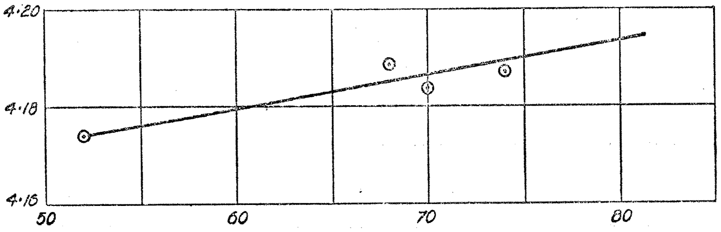

TABLE XXI.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d}{dv}\overline{pv}$.	γ.	β.
81	15·8	21·29	48·57	4·195	1·013	1·149	3·704
80	15·5	21·28	48·59	4·194	1·013	1·147	3·768
74	15·5	21·25	48·58	4·189	1·011	1·141	3·929
					Mean . .	1·145	3·800

§ 11. *Carbon Dioxide* (CO_2).

The gas was prepared from marble and hydrochloric acid. It was purified by being washed with water and passed over bicarbonate of potash and calcium chloride.

REGNAULT's value, 1·529, was taken as the specific gravity of the gas.

The experiments of ANDREWS afford material for calculating the term $1 + \frac{1}{p}\frac{d}{dv}\overline{pv}$. Using the results as tabulated by LANDOLT and BÖRNSTEIN (2nd edition, p. 83), the term has the value 1·007 for atmospheric pressure and temperatures between 0° and 30°.

The following table gives the results of the experiments, the pressure of the gas being in each case that of the atmosphere.

TABLE XXII.

t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d}{dv}\overline{pv}$.	γ.	β.
18·2	37·92	48·84	1·529	1·007	1·306	
18·1	37·97	48·83	..	..	1·311	
17·4	37·92	48·75	..	..	1·312	
14·7	37·65	48·53	..	..	1·304	
11·9	37·48	48·28	..	..	1·306	
12·6	37·57	48·34	..	..	1·310	
				Mean . . .	1·308	1·224

Previous determinations of the ratio of the specific heats of carbon dioxide have given the following results:—

t.	γ.	Observer.
	1·291	CAZIN ('Ann. de Chim.,' 56, 206)
19°	1·305	RÖNTGEN ('Pogg. Ann.,' 148, 580)
20–25	1·292	DE LUCCHI ('Nuov. Cim.,' 11, 11)
0	1·311	WÜLLNER ('Wied. Ann.,' 4, 321)
100	1·282	"
9–34	1·265	MÜLLER ('Wied. Ann.,' 18, 94)
	1·29	JAMIN and RICHARD ('Comptes Rendus,' 71, 336)

All these observers have used the equations of a perfect gas. My own result would be 1·299 without the correction for deviation from BOYLE's Law.

§ 12. *Carbon Bisulphide* (CS_2).

The liquid was first distilled from lime over which it had stood several days. It was then shaken repeatedly with mercury, dried with calcium chloride, and redistilled.

As the determinations of the absolute vapour density give an unsatisfactory curve, two of the experiments giving values rather more than a tenth per cent. away from the curve through the other three, a separate experiment was made to find the relative densities in the usual way. The results of this experiment are shown in Table XXIII., and fig. 8.

TABLE XXIII.

T.	p.	v.	pv/T.
286·7	123·3	118·6	49·56
	170	85·8	49·45
	197·9	73·6	49·38

Fig. 8.

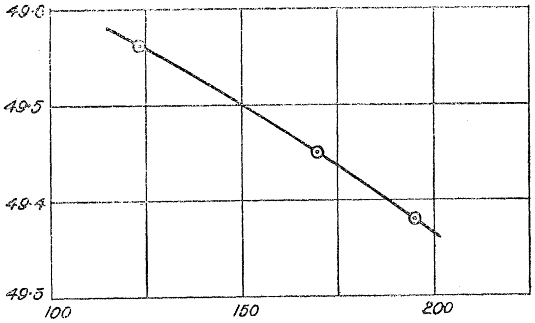

Table XXIV. gives the results of the vapour-density determinations. The numbers in the fourth column are taken from the curve in fig. 8, and when multiplied by the corresponding numbers in the third column should give a constant, if the two series of experiments are consistent. The products are shown in the last column.

Table XXIV.

p.	t.	ρ.	pv/T.	$pv\rho/\mathrm{T}$.
134	11·4	2·647	49·53	1311
147	11·6	2·644	49·50	1309
193	11·6	2·654	49·39	1310
125	12·4	2·643	49·56	1310
161	9·8	2·648	49·47	1310
			Mean	1310

The mean of the numbers in the last column of this table divided by the ordinate of the curve in fig. 8 for a given pressure, gives the best value of the vapour-density for that pressure. The fifth column of the table below was calculated in this way.

Table XXV.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d}{dv}\overline{pv}$.	γ.	β.
121	11·4	27·71	48·23	2·643	1·006	1·236	1·890
130	16	27·94	48·63	2·644	1·006	1·236	1·890
141	12·8	27·77	48·24	2·645	1·007	1·243	1·819
150	13·4	27·79	48·42	2·647	1·008	1·237	1·903
156	14	27·86	48·46	2·648	1·008	1·242	1·843
					Mean . . .	1·239	1·869

§ 13. *Sulphuretted Hydrogen* (H_2S).

The gas was prepared by warming antimony sulphide with hydrochloric acid. It was washed with water, and dried by being passed over calcium chloride.

An experiment to determine the deviation of the gas from Boyle's Law gave the following result :—

Table XXVI.

T.	v.	p.	$pv/$T.
291·8	38·67	967·8	128·2
	49·8	754·65	128·7
	64·07	587·85	129·0
	85·12	443·05	129·2
	102·2	369·5	129·4

These numbers give ·011 as the value of $\frac{1}{p}\frac{d}{dv}\overline{pv}$ at 760 millims.

The theoretical density 1·177 is used in the calculation of γ.

Three determinations of the velocity of sound at atmospheric pressure give the following results :—

Table XXVII.

t.	l.	l'.	ρ.	$1+\frac{1}{p}\frac{d}{dv}\overline{pv}$.	γ.	β.
17·8	43·31	48·78	1·177	1·011	1·321	
18	43·46	48·85	..	..	1·322	
18	43·42	48·83	..	..	1·321	
				Mean . . .	1·321	1·165

§ 14. *Ethyl Formate* ($HCOOC_2H_5$).

The ethyl formate used in the experiments was allowed to stand over anhydrous carbonate of potash and calcium chloride, and was then fractionated. This treatment made the boiling-point steady, but the substance is so readily decomposed, that the operation had to be repeated at times, and consequently the material used was not the same in all the experiments.

Every precaution was taken to keep the apparatus thoroughly dry inside and so prevent decomposition; but in spite of this the vapour-density results were not concordant enough to give a trustworthy curve. Hence it was necessary to make a determination of the relative densities.

The tables and figures have exactly the same meaning as the corresponding ones for carbon bisulphide. Table XXVIII. and fig. 9 exhibit the results of the relative density determination, Table XXIX. those of the absolute determinations, and Table XXX. gives the values found for γ and β.

TABLE XXVIII.

p.	t.	$\frac{pv}{t+273}$.
92	17·9	25·67
105	..	25·62
119	..	25·55
134	..	25·52
148	..	25·46

Fig. 9.

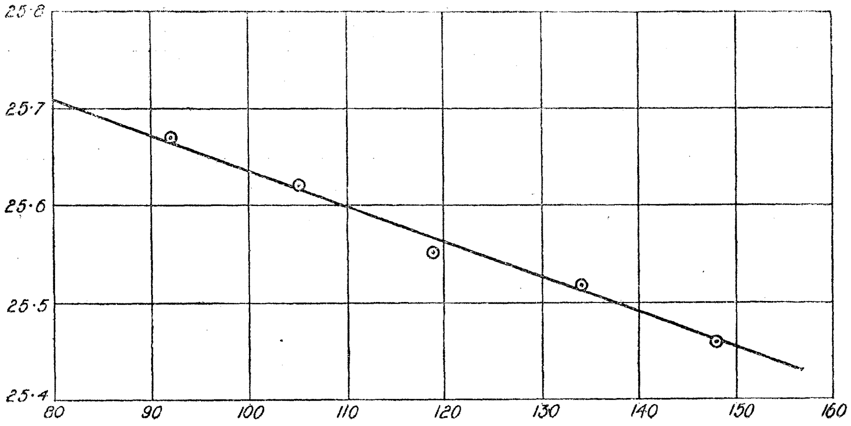

TABLE XXIX.

p.	t.	ρ.	$\frac{pv}{t+273}$.	$\frac{pv\rho}{t+273}$.
105	18	2·487	25·61	6368
109	17·8	2·489	25·59	6369
110	18·4	2·485	25·59	6359
131	18·2	2·498	25·52	6372
131	18·3	2·499	25·52	6377
149	18·6	2·498	25·45	6357
			Mean	6367

TABLE XXX.

p.	t.	l.	l'.	ρ.	$1+\frac{1}{p}\frac{d}{dv}\overline{pv}$.	γ.	β.
94	20·8	27·67	49·03	2·482	1·014	1·129	4·450
99	18·9	27·49	48·86	2·485	1·015	1·124	4·694
101	19·9	27·49	48·96	2·486	1·015	1·120	4·883
122	20·3	27·57	49·05	2·492	1·018	1·128	4·578
141	20·0	27·43	48·97	2·500	1·021	1·128	4·640
142	19·4	27·42	48·92	2·500	1·021	1·129	4·597
					Mean	1·125	4·640

§ 15. *Methyl Acetate* (CH_3COOCH_3).

Methyl acetate proved to be more troublesome than any of the other substances investigated, and it is with some hesitation that I venture to publish the results of my experiments on it. Time after time the liquid was shaken with calcium chloride and fractionated, but the boiling-point was never as steady as could be wished. One of the decomposition products is methyl alcohol, which has nearly the same boiling-point as methyl acetate itself, and cannot be removed by fractionation, so that it is hardly to be hoped that the final product was quite pure.

The experiments with the KUNDT apparatus, given below in Table XXXI., are not the only ones that were made. After each purification several experiments were made, and it was found that the wave-length of sound in the vapour gradually diminished—presumably in consequence of the gradual removal of methyl alcohol. The set given below were made on the particular sample that gave the shortest wave-length.

If the vapour-density determinations gave the true density of the material used in the velocity of sound experiments, a little impurity would have scarcely any effect on γ, but the vapour-density observations are specially liable to error. The quantity of methyl acetate used in an experiment is small—not more than a quarter of a gramme—and a very little moisture on the glass may bring about the decomposition of quite an appreciable percentage of the vapour. It is probably for this reason that the experimental error of the vapour-density observations is greater than usual, the divergence from the mean reaching 1 part in 400.

The tabulation of the results is the same as before. Table XXXI. and fig. 10 give the relative density determinations. Table XXXII. gives the absolute density results, and Table XXXIII. gives the values found for γ.

TABLE XXXI.

p.	t.	$\frac{pv}{t + 273}$.
85	18·9	33·58
105	..	33·38
117	..	33·35
127	..	33·28
137	..	33·20
153	..	33·09

Fig. 10.

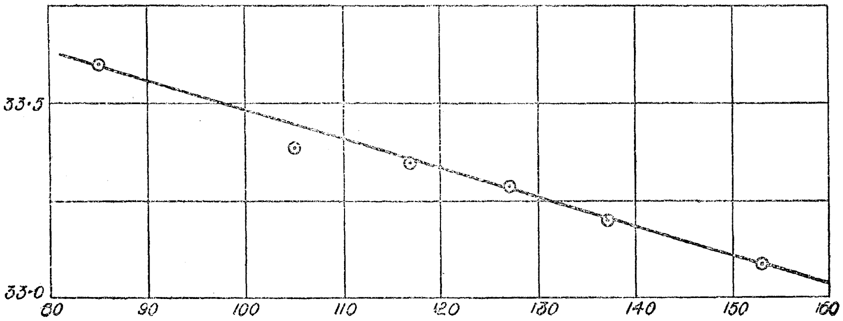

TABLE XXXII.

p.	t.	ρ.	$\frac{pv}{t + 273}$.	$\frac{pv\rho}{t + 273}$.
68	18·6	2·483	3372	8373
71	18·1	2·488	3368	8379
82	18·8	2·486	3362	8360
87	17·4	2·485	3357	8343
92	17·6	2·498	3353	8375
97	18	2·491	3350	8345
100	17·7	2·506	3347	8385
100	16·8	2·503	3347	8375
102	16·6	2·500	3346	8364
114	18·4	2·509	3337	8360
			Mean . .	8366

TABLE XXXIII.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d}{dv}\overline{pv}$.	γ.	β.
93	18·2	27·51	48·82	2·496	1·019	1·137	4·234
102	19·7	27·57	48·96	2·501	1·020	1·139	4·172
103	19·8	27·51	48·97	2·502	1·020	1·134	4·365
104	18·3	27·48	48·84	2·502	1·021	1·139	4·194
86	9·05	27·10	48·03	2·492	1·018	1·137	4·212
					Mean . .	1·137	4·235

§ 16. *Silicon Tetrachloride* ($SiCl_4$).

Silicon tetrachloride is much more unstable even than the two substances last described. It decomposes so readily in the presence of moisture that white fumes of silica are given off if the bottle containing the liquid is left open.

The KUNDT apparatus was easily dried, so there was probably no appreciable decomposition in the velocity of sound experiments, but the vapour-density apparatus was more difficult to keep from contact with moist air, and at the end of the set of experiments a slight dimming of the glass from the deposit of silica showed that the attempt to keep out moisture had not been entirely successful.

TABLE XXXIV.

p.	t.	ρ.
84	14	5·797
88	14·1	5·810
106	14·1	5·848
110	13·6	5·875
126	16	5·879
138	16·1	5·878

Fig. 11.

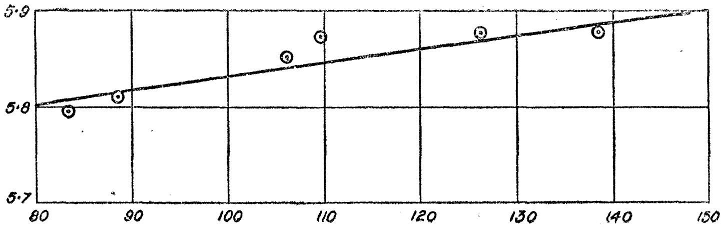

TABLE XXXV.

p.	t.	l.	l'.	ρ.	$1+\frac{1}{p}\frac{d}{dv}\overline{pv}$.	γ.	β.
105	13·9	17·82	48·46	5·838	1·024	1·138	4·289
118	14	17·75	48·4	5·857	1·026	1·135	4·453
128	13·8	17·62	48·45	5·871	1·028	1·124	4·975
141	13·9	17·60	48·46	5·888	1·031	1·127	4·898
144	14·8	17·54	48·53	5·891	1·032	1·119	5·311
					Mean	1·129	4·585

§ 17. *Discussion of the Results.*

As many of the above gases are closely related to those included in my former paper, the whole of the results of the two series are included in one table.

TABLE XXXVI.

Name.	Formula.	γ.	β.	$\frac{\beta}{n}$	$\frac{\beta+1}{n}$
Methane	CH_4	1·313	1·129	·226	·426
Methyl chloride	CH_3Cl	1·279	1·506	·301	·501
Methyl bromide	CH_3Br	1·274	1·573	·314	·514
Methyl iodide	CH_3I	1·286	1·597	·319	·519
Methylene chloride	CH_2Cl_2	1·219	2·175	·435	·635
Chloroform	$CHCl_3$	1·154	3·506	·701	·901
Carbon tetrachloride	CCl_4	1·130	4·411	·882	1·082
Ethane	C_2H_6	1·182	2·659	·332	·457
Ethyl chloride	C_2H_5Cl	1·187	2·838	·355	·479
Ethyl bromide	C_2H_5Br	1·188	2·809	·351	·476
Ethylene chloride	$C_2H_4Cl_2$	1·137	4·184	·523	·648
Ethylidene chloride	$C_2H_4Cl_2$	1·134	4·243	·530	·655
Propane	C_3H_8	1·130	4·427	·402	·493
Normal propyl chloride	C_3H_7Cl	1·126	4·493	·408	·499
Isopropyl chloride	C_3H_7Cl	1·127	4·465	·406	·497
Isopropyl bromide	C_3H_7Br	1·131	4·415	·401	·492
Ethylene	C_2H_4	1·250	1·740	·290	·457
Vinyl bromide	C_2H_3Br	1·198	2·715	·452	·619
Allyl chloride	C_3H_5Cl	1·137	4·023	·447	·558
Allyl bromide	C_3H_5Br	1·145	3·800	·422	·533
Ethyl formate	$H.COOC_2H_5$	1·124	4·640	·422	·513
Methyl acetate	CH_3COOCH_3	1·137	4·235	·385	·476
Sulphuretted hydrogen	SH_2	1·321	1·165	·388	·722
Carbon dioxide	CO_2	1·308	1·224	·408	·741
Carbon bisulphide	CS_2	1·239	1·869	·623	·956
Silicon tetrachloride	$SiCl_4$	1·129	4·585	·917	1·117

My former conclusion that monohalogen derivatives of the same paraffin have the same γ can now be stated in more general terms. The two allyl compounds show that it is not restricted to saturated hydrocarbons, and the equality of γ of ethylene and ethylidene chlorides extends it to isomeric dihalogen derivatives. Hence, so far as the experiments have gone, we can say that without any exception *corresponding halogen derivatives of the same hydrocarbon have the same ratio of the specific heats.*

Similarly it appears that the equality of γ for the two propyl chlorides is not an isolated fact, for two other pairs of isomeric bodies, viz., ethylene and ethylidene chlorides and methyl acetate and ethyl formate prove to have the same γ. As I have mentioned above, there is some doubt about the results for the two last mentioned, but at present the balance of evidence is in favour of the statement that *isomeric compounds have the same* γ.

In the case of the paraffins ethane and propane, it was shown in my former paper that one H can be replaced by a halogen without altering the value of γ, but that the introduction of a halogen into methane causes a fall in γ. We see now that the unsaturated gas ethylene behaves in the same way as methane, for the γ of vinyl bromide is markedly lower than that of ethylene. Thus the possibility of interchange of hydrogen with a halogen without altering γ is not general, a fact that is brought out still more clearly by a consideration of the higher substitution products.

It was shown by STRECKER* that hydrochloric, hydrobromic and hydriodic acids all have nearly the same γ as hydrogen, namely 1·4, whilst the γ's of chlorine, bromine, iodine and iodine chloride all lie near 1·3. Hence in this case one halogen can be put in the place of hydrogen without affecting γ, but the introduction of a second halogen causes a large fall.

The paraffin derivatives show the same feature. *The second* Cl *introduced into the molecule invariably causes a large fall in* γ whether the first has done so or not. Thus, whilst ethyl chloride has the same γ as ethane, ethylene and ethylidene chlorides are 4 per cent. lower.

The methane substitution products are volatile enough to allow the whole series to be investigated, and here we find that every successive chlorine atom introduced causes a fall in γ.

The work done on the last four gases in the table is only the beginning of a line of investigation, the completion of which would require an entire remodelling of my apparatus, so as to enable it to stand higher temperatures. The object of the experiments was to find whether other chemically analogous atoms are interchangeable in the same way as the halogens.

Although C and Si replace each other in many compounds, CCl_4 and $SiCl_4$ are not strictly analogous, for they violate the usual rule that the compound with the higher molecular weight has the higher boiling-point. They appear however to have the same γ.

---

* 'Wied. Ann.' vol. 13, p. 20, and vol. 17, p. 85.

The further investigation of the relations of carbon and silicon would be a matter of some difficulty, from the readiness with which the silicon compounds are decomposed.

Corresponding oxygen and sulphur compounds are numerous and stable, but most of the sulphur compounds have too high boiling-points to give a sufficiently dense vapour at the atmospheric pressure.

The value of γ for sulphuretted hydrogen was got for comparison with that found by other observers of water. Experiments made on water vapour have given the following results :—

Table XXXVII.

t.	γ.	Observer.
78	1·274	Beyme ('Beibl.,' vol. 9, p. 503)
94	1·33	Jäger ('Wied. Ann.,' vol. 36, p. 165)
100	1·321	Neyreneuf ('Ann. de Chim.,' vol. 9, p. 535)
103	1·277	De Lucchi ('Nuov. Cim.,' vol. 11, p. 11)
144–300	1·287	Cohen ('Wied. Ann.,' vol. 37, p. 628)

These are very discordant, but some of them seem to be of doubtful validity. Beyme made only a single experiment, and measured only three dust figures. De Lucchi used Clément and Desormes' method, with a receiver so small that, in the light of Röntgen's experiments, his result is probably too low. Neyreneuf and Cohen both assumed that the vapour obeys Boyle's Law, the latter observer trusting to superheating of the gas to justify the assumption. Jäger alone carried out his calculations in a manner that seems allowable, and his result is almost the same as I have found for sulphuretted hydrogen.

The two gases CO_2 and CS_2 have widely different values of the ratio of the specific heats, so that the possibility of interchange of O and S without altering γ does not at least extend to two atoms.

It is worth noticing that according to Regnault's results the molecular heat at constant pressure is nearly the same for the members of any one of the groups—H_2S and H_2O ; $(C_2H_5)_2S$ and $(C_2H_5)_2O$; $SiCl_4$ $SnCl_4$ and $TiCl_4$; so that it seems likely that the laws I have found to hold for the halogens will prove to hold for other groups of analogous elements.

Up to this point, only the relations of the γ's of the gases to each other have been discussed, though it is from their enabling us to calculate β that the values of γ are likely to prove ultimately most useful.

If two gases have the same γ, they have approximately the same β, that is, for a small rise of temperature the quantity of energy absorbed by the internal vibrations of the molecules bears the same ratio to the increase of kinetic energy of translation of the whole molecule in the two cases.

Thus, for instance, the molecules CH_3Cl, CH_3Br and CH_3I have the same energy absorbing power, from which it follows, with a high degree of probability, that the halogen atoms in these molecules, in spite of their great difference in mass, absorb the same share of the total energy. It is very improbable that if they did not, the redistribution of energy in the molecule on interchange of the halogens would result in the total capacity being unchanged. Similarly, we may infer from the behaviour of hydrogen, ethane, and propane that the chlorine atom may in some cases have the same energy absorbing power as the hydrogen it replaces.

An instance of another kind of interchange that can be made without disturbing the distribution of energy, is seen in the case of the two propyl chlorides and the two dichlorethanes. Trusting to graphic formulæ the chemist explains the difference between the two members of a pair as being due to a hydrogen changing places with a chlorine within the molecule, the configuration being in other respects unchanged.

The relation of methyl acetate to ethyl formate is explained in a somewhat similar way, for if we write the formula of ethyl formate in the form $CH_3—CH_2—O—CO—H$—we can convert it into that of methyl acetate by interchanging CH_2 and CO. Thus it appears that, if we can trust graphic formulæ to give information of this kind, groups may be interchanged without disturbing β. It would be of interest to carry out this point farther, and find whether one of the groups could be removed from the molecule, and the other put in its place without altering β. Has, for instance, methyl-ethyl oxide, which would be obtained by replacing CO in either of the above by CH_2, the same γ? It is probable that valuable information on the status of the radicle might be got by the determination of β for a number of suitably chosen compounds.

It appears then that a single atom of hydrogen, oxygen or carbon can in many cases be replaced by chlorine, sulphur and silicon respectively, without disturbing the distribution of energy in the molecule, but in no case investigated can the replacement be repeated without bringing about a large increase in β. Hence we conclude that an atom has not an intrinsic heat capacity which it carries with it unchanged into any gaseous molecule of which it forms part, but that it is affected by its neighbours. In other words β is not an additive quantity, for the configuration of the molecule plays a part in the distribution of energy.

My experiments would not be inconsistent with the supposition that the configuration is the sole feature that fixes the distribution, but until more definite evidence is obtained—especially with regard to the physical significance of radicles—this must remain no more than a suggestion.

It was pointed out many years ago by NAUMANN, when experimental evidence was scanty, that β divided by the number of atoms in the molecule was nearly equal to ·33. If this held generally, it would be an important fact, for it would point to something of the nature of BOLTZMANN's Theorem being true, and as the statement is sometimes quoted by writers, I have given the quotients in question in the fifth column of Table XXXVI. It will be seen that in many cases β/n shows a rough approximation to ·33, but no more. Even allowing for the exaggeration of the experimental error by the nature of the equation connecting β and γ, it cannot be said that the intramolecular energy is proportional to the number of atoms in the molecule. The paraffins themselves and their monohalogen derivatives show the closest approximation, but even in their case the quotient appears to increase as n increases.

This last fact and the extract below from an article by Professor J. J. THOMSON (WATTS, 'Dictionary of Chemistry,' vol. 1, p. 89), suggest another relation among the β's that looks more promising. The extract in question is as follows:—"Though there is strong evidence against the truth of the theorem (*i.e.*, BOLTZMANN'S Theorem) in this form, and the mathematical proof of it is unsatisfactory, yet a very special case of it is probably true, viz., that if we have a molecule consisting of n atoms approximately symmetrically arranged (that is, if the distance between a particular pair of atoms is not always very much less than the distances between the other pairs), then the ratio of the mean total kinetic energy of the molecule to the energy due to the translatory motion of the centre of gravity is proportional to n, the number of atoms in the molecule."

If then the molecules of the gases I have investigated are symmetrical in the above sense, we ought to find $(\beta + 1)/n$ constant. Looking down the last column of the table it will be seen that, though this is by no means the case throughout, yet if we confine ourselves to the paraffins and their derivatives that have not more than one halogen atom in the molecule, there is a very striking agreement.

The mean of the eleven quotients so defined is ·493. Methane, as we have already seen, falls out of the series, and here it diverges to the extent of 13 per cent., which is equivalent to a divergence of about 3 per cent. in γ. The γ of ethane would have to be about 1 per cent. lower to give complete agreement. In the case of all the rest the divergence is well within the probable experimental error.