XXXV.—*The Firing of Gases by Adiabatic Compression. Part IV. The Ignition-Points of Mixtures of Electrolytic Gas with Carbon Dioxide. Ratio of the Specific Heats for Carbon Dioxide.*

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As the addition of a monatomic gas to the diatomic constituents of electrolytic gas gave such interesting results under adiabatic compression, it was thought advisable to investigate the conditions for ignition of a series of mixtures containing a triatomic gas. Carbon dioxide appeared to be the most suitable gas for this purpose, and mixtures of the general formula $2\text{H}_2 + \text{O}_2 + x\text{CO}_2$ were prepared, and the conditions for explosion under adiabatic compression were investigated. It was not possible to determine the conditions of explosion of electrolytic gas diluted with carbon dioxide to the same extent as with nitrogen, argon, etc., owing to the fact that the ratio of the specific heats for this triatomic gas is small, and therefore considerable compression is required in order to fire the gas when very much diluted; the final volume of the mixture in such cases is small, and the error in obtaining its value relatively large.

A discussion of the figures given by various experimenters for the value of γ for carbon dioxide is given after the experimental part of this paper; it is necessary to state here that such figures lead, when applied to the experimental data, to a series of ignition-points which do not agree with those obtained from the argon series (see preceding paper). Taking the formula given by Lewis and Randall for the specific heat at constant pressure, namely,

$$C_p = 7.0 + 0.0071T - 0.00000186T^2,$$

we can, as shown in the previous paper, using the method of mixtures, obtain a value for the ignition-point. For instance, from table I below it is seen that the mixture $2\text{H}_2 + \text{O}_2 + \text{CO}_2$ explodes at $V_2 = 20.8$ when $T_1 = 288.7$. This should give an ignition-point of 532° , corresponding with that given by the corresponding argon mixture, $2\text{H}_2 + \text{O}_2 + \text{A}$. Calculating from the above formula, $C_v = 8.21$ and $\gamma = 1.241$. Using these figures and calculating in the usual manner, we get the final temperature of the mixture = 793 abs. or 520° . Thus it would appear that the addition of carbon dioxide to the extent of 33 per cent. of the electrolytic gas taken has no effect on the ignition-point of the mixture. Judging by the effects of the addition of other gases, this is not probable, and evidently the value of γ used is too small. The experimental data, then, were

used as in Part III, dealing with nitrogen and hydrogen, to obtain values for γ and the molecular heat at constant volume for carbon dioxide.

Before proceeding to deal with the explosion data it was thought desirable to see whether any chemical action took place between the gases in the mixture beyond the combination of hydrogen and oxygen to form water. Berthelot (*Ann. Chim. Phys.*, 1898, [vii], **14**, 167), although he gives no experimental details, states that if a mixture of oxygen, hydrogen, and carbon dioxide, the two former in the proportion to form water, is ignited and exploded, the hydrogen is completely burnt to water without any action on the carbon dioxide taking place. If the hydrogen is by itself or has insufficient oxygen with it to produce complete oxidation, then some of the carbon dioxide is reduced to carbon monoxide. This fact is well known, but in support the work of Dixon (T., 1886, **49**, 94) and of Boudouard (*Bull. Soc. chim.*, 1901, [iii], **25**, 485) may be quoted. It was thought well, however, to investigate the case under the actual conditions of the adiabatic compression.

Hydrogen and carbon dioxide were mixed in different proportions, and the mixed gas compressed to temperatures roughly corresponding with the ignition-points of the $2\text{H}_2 + \text{O}_2 + x\text{CO}_2$ mixtures, in which the hydrogen and carbon dioxide were in the same relative proportion to one another. After compression the gases were withdrawn from the explosion chamber and analysed in a Bone and Wheeler gas analysis apparatus. The details are as follows:

(1) The mixture $2\text{H}_2 + \text{CO}_2$ was compressed to $V_2 = 18.0$, T_1 being 287.9 ; thus $T_2 = 540^\circ$ roughly. On analysis the percentage composition was:

	Before compression.
$\text{CO}_2 = 33.02$	$\text{CO}_2 = 33.04$
$\text{H}_2 = 66.9$	$\text{H}_2 = 66.96$
$\text{CO} = 0.08$	—

(2) $\text{H}_2 + \text{CO}_2$ compressed to $V_2 = 13.4$, T_1 being 287.3 ; thus T_2 was roughly 557° (see table III below). Analysis:

After compression.	Before compression.
$\text{CO}_2 = 47.51$	47.55
$\text{H}_2 = 52.43$	52.45
$\text{CO} = 0.06$	—

(3) $2\text{H}_2 + 5\text{CO}_2$ compressed to $V_2 = 5.0$, T_1 being 286.9 , T_2 working out at about 720° , the value of γ for carbon dioxide being doubtful at this temperature. Analysis:

After compression.	Before compression.
$\text{CO}_2 = 68.9$	69.1
$\text{H}_2 = 31.0$	30.9
$\text{CO} = 0.1$	—

In these analyses the average amount of carbon monoxide found was only 0.08 per cent., a figure exceedingly small; so small, in fact, as to be scarcely outside the error of observation in conducting the analyses.

These analyses might usefully be compared with one of a mixture, $2\text{H}_2 + \text{O}_2$, compressed to a temperature just under the ignition-point (520°):

After compression.	Before compression.
$\text{H}_2 = 66.68$	66.70
$\text{O}_2 = 33.26$	33.29
$\text{CO} = 0.06$	=

Here, again, a minute quantity of carbon monoxide appears to be present; but in this case it can come only from a partial burning of the lubricant, or charring of the leather washer fitted to the piston. One may conclude, therefore, that at the temperatures under consideration the amount of reduction of the carbon dioxide effected by the hydrogen, if any, is extremely small, and is not sufficient to affect the action of a mixture, $2\text{H}_2 + \text{O}_2 + x\text{CO}_2$, in the cylinder.

After any explosion, however, carbon monoxide is always found in the cylinder, along with carbon dioxide. This, as already explained (Dixon and Crofts, *loc. cit.*, p. 2040), is an after-effect of the explosion, and is produced from the lanoline as the piston is being pushed back. The subjoined analyses taken after the explosion of a mixture, $2\text{H}_2 + \text{O}_2 + 3\text{CO}_2$, throw light on this point, and confirm the statement made above that in the mixture the hydrogen and oxygen burn completely to water. Four different experiments were performed. In (a) a large amount of lanoline was used; the amounts were reduced in (b) and (c), and in (d) none at all was put on the leather, which, of course, had been used for some time, and was well impregnated with lubricant. The figures given are calculated on the original amount of gas, the final volume being reckoned as 50 per cent. of the original, and the initial composition is given under (e) for purposes of comparison. After removal of carbon monoxide some gas remained, which exploded when mixed with oxygen and sparked. This is termed "hydrocarbon" in the analyses, and proceeds from the lanoline:

	(a.)	(b.)	(c.)	(d.)	(e.)
CO_2	43.9	45.3	46.7	47.3	49.3
CO	2.3	1.3	0.9	0.5	—
Hydrocarbon } and Residual N_2 }	 3.8	 3.4	 2.4	 2.2	 1.2

These figures, as they stand, need correction; they show fairly correctly the amounts of monoxide formed, but they make it appear

that large amounts of dioxide are attacked. This, however, is not the case, as additional gas is formed by the explosion, as shown as follows: The original volume of gas, $V_1=37.7$, and the pressure of this gas was noted by the manometer; after explosion the volume of gas left by this particular mixture (50 per cent. of carbon dioxide) should be $\frac{37.7}{2}=18.85$ at the same pressure; actually,

however, three successive experiments under conditions (*d*) gave this amount as 19.4, 19.4, and 19.5; taking the value 19.4 as correct, we have by the analysis that 94.6 per cent. (2×47.3) of this is carbon dioxide, $\frac{94.6}{100} \times 19.4 = 18.55$, and this in turn is 49.2 per cent. of 37.7, the original volume of gas taken. This figure, 49.2 per cent. compared with 49.3 per cent.—the figure given for the original gas under (*e*) above—shows that little, if any, reduction of the dioxide has taken place.

Subjoined are the records of experiments conducted to find the ignition-points of mixtures $2H_2 + O_2 + xCO_2$ (*N* denotes a non-explosion and *X* an explosion):

TABLE I.

t_1 .	V_2 .	Result.	t_1 .	V_2 .	Result.
15.5	18.8	X	15.4	20.3	X
15.6	21.8	N	15.6	20.8	N
15.7	19.8	X	15.6	20.5	X
15.8	20.8	N	15.7	20.7	X
15.9	20.3	X			

Ignition-point is derived from $288.7 \left[\frac{377}{20.7} \right]$ (see below).

TABLE II.

t_1 .	V_2 .	Result.	t_1 .	V_2 .	Result.
15.0	16.5	N	15.4	16.3	N
15.1	16.0	X	15.4	16.1	X
15.1	16.3	N	15.5	16.2	X
15.2	16.1	X			

Ignition-point is derived from $288.5 \left[\frac{377}{16.2} \right]$.

TABLE III.

t_1 .	V_2 .	Result.	t_1 .	V_2 .	Result.
15.2	11.8	X	15.6	13.5	N
15.3	12.8	X	15.7	13.4	X
15.4	13.8	N	15.8	13.6	N
15.5	13.3	X			

Ignition-point is derived from $288.7 \left[\frac{377}{13.4} \right]$.

TABLE IV.

t_1 .	V_2 .	Result.	t_1 .	V_2 .	Result.
15.3	9.9	X	15.5	11.0	X
15.3	10.1	X	15.5	11.6	N
15.4	11.0	X	15.6	11.3	X
15.5	12.0	N	15.6	11.4	N

Ignition-point is derived from $288.6 \left[\frac{377}{11.3} \right]$.

These experimental data were now used to obtain values for the ratio of the specific heats; the mode of calculation is similar to that set out in the previous paper on the specific heats of nitrogen and hydrogen, and need not be detailed again.

The assumption is made that mixtures of electrolytic gas with carbon dioxide have the same ignition-point as corresponding mixtures with argon. This assumption, although perhaps not absolutely correct, does not appear to be wide of the mark.

(1) Mixture $2\text{H}_2 + \text{O}_2 + \text{CO}_2$ explodes at $V_2=20.7$ when $T_1=288.7$. The corresponding argon mixture has an ignition-point of $532^\circ=805$ abs.

From this, for CO_2 , $\gamma=1.254$ and $C_v=7.815$.

(2) Mixture $2\text{H}_2 + \text{O}_2 + 2\text{CO}_2$ explodes at $V_2=16.2$ when $T_1=288.5$. The corresponding argon mixture has an ignition-point of 545° or 818 abs.

From this, for CO_2 , $\gamma=1.253$ and $C_v=7.847$.

(3) Mixture $2\text{H}_2 + \text{O}_2 + 3\text{CO}_2$ explodes at $V_2=13.4$ when $T_1=288.8$. The corresponding argon mixture has an ignition-point of 557° or 830 abs.

From this, for CO_2 , $\gamma=1.252$ and $C_v=7.878$.

(4) Mixture $2\text{H}_2 + \text{O}_2 + 4\text{CO}_2$ explodes at $V_2=11.3$ when $T_1=288.6$. The corresponding argon mixture has an ignition-point of 570° or 843 abs.

From this, for CO_2 , $\gamma = 1.251$ and $C_v = 7.909$.

Tabulating these results, and using t_1 as 15 approximately:

Temperature-interval.	Mean value of γ .	Mean value of C_v .
15°-532°	1.254	7.815
15 -545	1.253	7.847
15 -557	1.252	7.878
15 -570	1.251	7.909

These figures cannot well be compared with those of other observers owing to the fact that rapid changes of temperature and pressure are going on at the same time. Many experiments have been conducted on carbon dioxide at ordinary temperatures and pressures; perhaps the most trustworthy are those of Lummer and Pringsheim (*Ann. Phys. Chem.*, 1898, [iii], **64**, 553), who give for γ the value 1.2995. Makower (*Phil. Mag.*, 1903, [vi], **5**, 226) gives $\gamma = 1.307$. Moody (*Physikal. Zeitsch.*, 1912, **13**, 383) finds $\gamma = 1.3003$. Evidently the figure is very close to 1.30.

For the specific heat at constant volume, under ordinary conditions of temperature and pressure there are few direct determinations. Joly (*Proc. Roy. Soc.*, 1894, **55**, 390) gives an equation for the specific heat, from which the molecular heat C_v works out at 7.3 (at a pressure of one atmosphere). This is higher than the figure derived from the value for C_p found by other observers, as is also evident from the fact that if in the equation $C_v = \frac{1.985}{\gamma - 1}$ we substitute 1.3 for γ , then $C_v = 6.62$.

The effect of rise of temperature alone has been studied by many observers. In all cases a decrease in the value of γ with rise of temperature has been found, and presumably an increase in the value of C_v (for references see above). In addition, Fürstenau (*Ann. Physik*, 1908, [iv], **27**, 735), by measuring the wave-lengths of sound, found $\gamma = 1.2506$ at 484.5° and 1.3008 at room temperature; taking the mean temperature of the compressed mixture $2\text{H}_2 + \text{O}_2 + \text{CO}_2$ as 273° , Fürstenau's experiments would give an approximate value 1.284.

The effects of pressure have not received so much careful study. Joly (*loc. cit.*) finds an increase in C_v up to a certain density, beyond which there is a decrease; the value of γ varies inversely with this. Under a pressure of 26 atmospheres, which is roughly the mean obtained in compressing the mixture $2\text{H}_2 + \text{O}_2 + \text{CO}_2$, Joly's equation gives $C_v = 7.4$. Amagat (*Compt. rend.*, 1895, **121**, 802), by the pressure method, finds an increase in the value of γ , as also does Thibaut (*Ann. Physik*, 1911, [iv], **35**, 373).

Worthing (*Phys. Rev.*, 1911, **33**, 217) investigated the changes

in value of γ under varying conditions of temperature and pressure; for example:

At $P = 7.78$ atmos.	$= 1.338$ at 0.2°
	$= 1.310$ „ 31
	$= 1.296$ „ 50
	$= 1.256$ „ 98.5
At $P = 28.52$ atmos.	$= 1.702$ „ 0.2
	$= 1.499$ „ 31
	$= 1.448$ „ 50
	$= 1.327$ „ 98.5

It is evident, therefore, that the effects of temperature and pressure work against one another in the case of the ratio γ .

For the combined effects of rise of temperature and pressure on the value of C_v , the explosion method of Mallard and Le Chatelier (*Ann. des Mines*, 1884, **4**, 378) is in its conditions somewhat comparable to the present method. These observers ignite, by means of a spark, an explosive mixture of gases, and observe the pressure generated by the explosion; knowing the amount of heat generated by the chemical action, one can, by means of the gas equation $PV = RT$, easily calculate the specific heats. In such experiments both temperature and pressure rise suddenly to high values, the maximum temperature being much higher than the ignition-points found in the present series of experiments. Mallard and Le Chatelier give a linear formula $6.5 + 0.00387t$ for mean C_v in the case of carbon dioxide; and later, Le Chatelier (*Compt. rend.*, 1887, **104**, 1780) gives $C_v = 6.5 + 0.0037T$. Langen (*Mitteilungen über Forschungsarbeiten auf dem Gebiete des Ingenieurwesens*, 1903, 8), who improved on the method, gives mean $C_v = 6.7 + 0.0026t$. More recently Pier (*Zeitsch. Elektrochem.*, 1909, **15**, 536; 1910, **16**, 897), still further improving on the method of estimating the pressure produced by the explosion, gives:

$$C_v = 6.8 + 3.3 \times 10^{-3}t - 0.95 \times 10^{-6}t^2 + 0.1 \times 10^{-9}t^3.$$

This equation gives results which agree very fairly with those deduced from the value of C_p (by using the relation $C_p - C_v = 1.985$) found by Holborn and Henning (*Ann. Physik*, 1907, [iv], **23**, 809) by the Regnault method.

In Part III. (p. 293) reference was made to work conducted by Clerk and by Hopkinson on the adiabatic compression of air and of carbon dioxide. The latter states (*Brit. Assoc. Reports*, 1910, 199) that the values obtained by him for C_v in the case of carbon dioxide are close to those deduced from Swann's results for C_p by extrapolation. Swann's results, both for air and for carbon dioxide, are higher than those of other observers who have employed the same method; for example, for carbon dioxide between 0° and 550° Swann's figures would give $C_v = 9.5$, which

value can be compared with those tabulated below. It should be mentioned again that Hopkinson assumed that the value of γ remained constant during the course of his experiments.

Finally, Lewis and Randall, as already stated, in considering all these figures, drew the conclusion that $C_p = 7.0 + 0.0071T - 0.00000186T^2$, from which, in view of the data employed, we may deduce $C_v = 5.0 + 0.0071T - 0.00000186T^2$.

The figures given by various observers for the mean value of C_v between 0° and 550° (the average final temperature of the mixtures given in this paper) are given below:

Mallard and Le Chatelier	8.628
Le Chatelier	8.527
Langen	8.13
Pier	8.344
Holborn and Henning.....	8.415
Fürstenau (about)	7.0
Joly	7.4
Lewis and Randall	8.191
Crofts.....	7.862

The first four figures are obtained from explosion methods; they are comparatively high, but not higher than that obtained by Holborn and Henning using Regnault's stream method to find C_p . Adiabatic methods give low figures, although not low in comparison with Joly's direct observation of C_v . Where there is such considerable variation in the values found by different experimenters and in the different conditions under which the various experiments were performed, it is of little value to push comparisons very far. At least it can be said that the values obtained by the present method are consistent and probable.

The four values found can be well expressed by means of the linear formula $C_v = 6.6 + 0.0023t$; they do not, however, cover a large range of temperature, the maximum being 532° in the first case and 570° in the last.

Temperature- interval.	C_v calculated.	C_v observed.	Difference. Per cent.
15° – 532°	7.823	7.815	–0.1
15 –545	7.853	7.847	–0.08
15 –557	7.881	7.878	–0.04
15 –570	7.911	7.909	–0.03

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