

The Internal Energy of Inflammable Mixtures of Coal-gas and Air after Explosion.

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The results of experiments upon the heat lost by radiation and by conduction during the explosion and subsequent cooling of inflammable gaseous mixtures have been recorded in previous papers.* In the first section of the present paper the experimental results for mixtures of coal-gas and air of various strengths have been combined, and an empirical law of cooling formulated.

In the second section of the paper the combined results have been applied to the estimation of the internal energy of the exploded mixtures at the maximum temperatures developed and at various stages during cooling. A study of the internal energy values for the different mixtures so obtained appears to throw into fair perspective the various causes responsible for the so-called "suppression of heat" in gaseous explosions—or, at any rate, in explosions of mixtures of coal-gas and air.

As is well known, the main theories which have been put forward to account for the low pressures developed are—

- (i) Increase of specific heat of the products of combustion with temperature (MM. Mallard and Le Chatelier). Under this head may be included such dissociation as may occur, since it would naturally be included in all specific heat measurements ;
- (ii) Incomplete combustion (Sir Dugald Clerk) ; and
- (iii) Heat loss to the walls of the containing vessel (Hirn).

The results given in this paper appear to show definitely that all these are important factors in limiting the maximum pressures developed ;† and they enable a quantitative estimate to be made as to their relative importance in the various mixtures experimented upon.

Results of Experiments.

Full details of the experimental methods employed in the determination of the radiation and conduction losses will be found in the papers already

* 'Phil. Trans.,' A, vol. 211, p. 375 ; 'Phil. Mag.,' January, 1920, p. 66, and 'Phil. Mag.,' September, 1920, p. 318.

† Sir Dugald Clerk, who put forward the theory of continued combustion in 1886, was not of opinion that it was the only cause limiting the pressure developed. He states very definitely that in his opinion the factors operating were complex. ('Proc. Inst. C. E.,' March, 1886.)

referred to. It will be convenient, however, to describe them here very briefly. The gaseous mixtures were contained in a cylindrical cast-iron vessel 30 cm. in diameter and 30 cm. in length, and were fired by means of an electric spark in the centre of the vessel. Continuous records of the pressure and of the heat loss during explosion and subsequent cooling were taken simultaneously. The radiation measurements are the mean of three sets of measurements made with the recording apparatus in three different positions on one of the end-covers of the explosion vessel, and it is believed that they give very approximately the mean value over the whole vessel. These values multiplied by the area of the interior surface of the vessel (4380 sq. cm.) should therefore give the total radiation loss fairly accurately. The conduction loss measurements are the average over a large portion of one of the end-covers. It cannot be stated with confidence that these measurements give an accurate indication of the mean value of the conduction loss over the entire surface of the vessel, but it is thought that they approximate sufficiently closely to this value to enable a fairly reliable estimate of the total conduction loss to be made.

The curves in figs. 1, 2, and 3 give the mean gas temperature and the

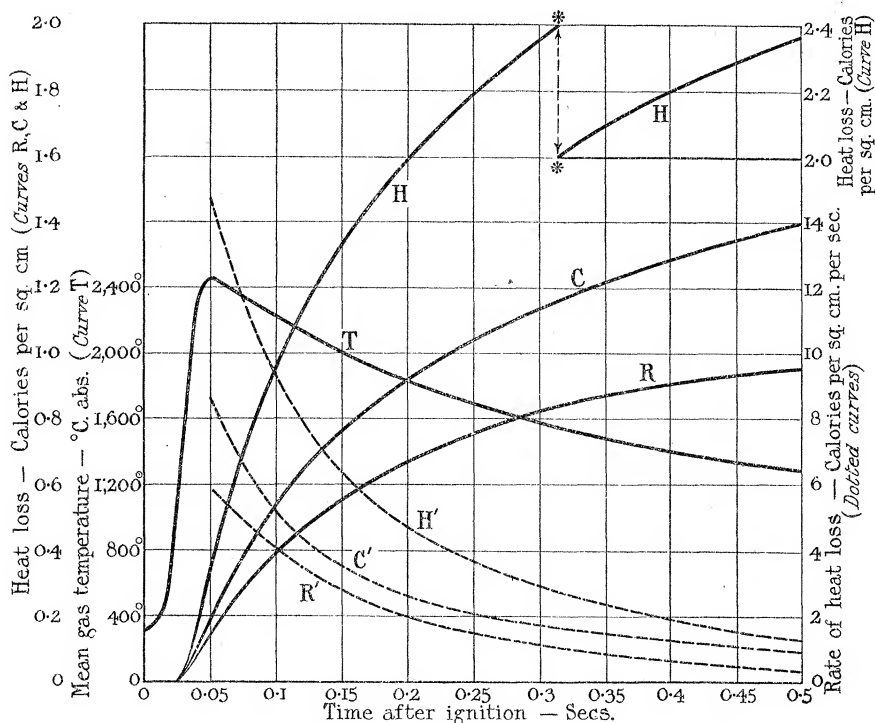


FIG. 1.—Heat-loss in 15 per cent. mixture coal-gas and air.

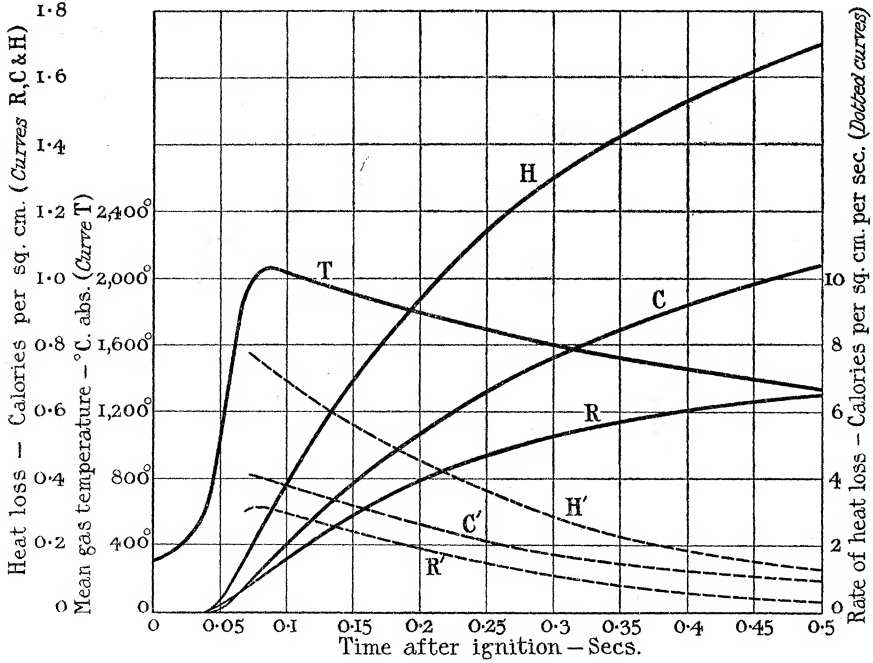


FIG. 2.—Heat-loss in 12.4 per cent. mixture coal-gas and air.

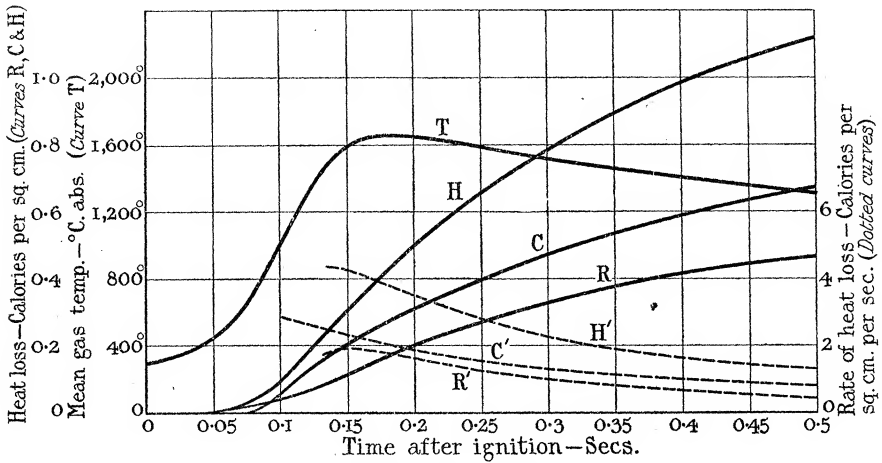


FIG. 3.—Heat-loss in 9.7 per cent. mixture coal-gas and air.

mean radiation and conduction losses per square centimetre of wall surface at various times after ignition in 15 per cent., 12.4 per cent., and 9.7 per cent. mixtures respectively. The T-curves give the mean gas temperature; the R-curves the mean radiation loss per square centimetre, the C-curves the mean conduction loss per square centimetre, and the H-curves the mean

total loss (*i.e.*, the radiation *plus* the conduction loss) per square centimetre. The dotted curves are the differentials of the heat loss curves (R, C, and H) and give the rate of heat loss (radiation, conduction and total) per square centimetre of wall surface per second. The data from which these curves have been drawn are given in Tables I, II, and III. The Tables also show the proportion of the heat of combustion of the coal-gas originally in the vessel which has been lost by radiation and conduction at various stages during cooling.

Table I.—Heat Loss in a 15 per cent. Mixture of Coal-Gas and Air. Heat of Combustion of Coal-Gas in Vessel = 16,300 calories.

Time after ignition (secs.).	Mean gas temperature (° C. abs.).	Heat loss per sq. cm. of surface.			Heat loss expressed as a percentage of the heat of combustion of the coal-gas.		
		Conduction.	Radiation.	Total.	Conduction.	Radiation.	Total.
0·05	2440 (max. temp.)	0·19	0·14	0·33	5·1	3·8	8·9
0·1	2220	0·54	0·39	0·93	14·4	10·4	24·8
0·15	2020	0·76	0·56	1·32	20·3	15·0	35·3
0·2	1840	0·92	0·67	1·59	24·5	17·9	42·4
0·25	1710	1·04	0·76	1·80	27·7	20·3	48·0
0·3	1600	1·13	0·83	1·96	30·0	22·2	52·2
0·4	1430	1·29	0·91	2·20	34·4	24·3	58·7
0·5	1300	1·41	0·96	2·37	37·6	25·6	63·2

Table II.—Heat Loss in a 12·4 per cent. Mixture of Coal-Gas and Air. Heat of Combustion of Coal-Gas in Vessel = 13,500 calories.

Time after ignition (secs.).	Mean gas temperature (° C. abs.).	Heat loss per sq. cm. of surface.			Heat loss expressed as a percentage of the heat of combustion of the coal-gas.		
		Conduction.	Radiation.	Total.	Conduction.	Radiation.	Total.
0·08	2050 (max. temp.)	0·17	0·14	0·31	5·5	4·5	10·0
0·1	2030	0·21	0·18	0·39	6·8	5·8	12·6
0·15	1920	0·38	0·3	0·68	12·5	9·7	22·2
0·2	1800	0·53	0·4	0·93	17·4	13·0	30·4
0·25	1700	0·67	0·48	1·15	21·7	15·6	37·3
0·3	1610	0·77	0·53	1·30	25·0	17·2	42·2
0·4	1460	0·93	0·61	1·54	30·2	19·8	50·0
0·5	1330	1·05	0·66	1·71	34·0	21·4	55·4

Table III.—Heat Loss in a 9·7 per cent. Mixture of Coal-Gas and Air. Heat of Combustion of Coal-Gas in Vessel = 10,600 calories.

Time after ignition (secs.).	Mean gas temperature (° C. abs.).	Heat loss per sq. cm. of surface.			Heat loss expressed as a percentage of the heat of combustion of the coal-gas.		
		Conduction.	Radiation.	Total.	Conduction.	Radiation.	Total.
0·18	1660 (max. temp.)	0·26	0·17	0·43	11·0	7·0	18·0
0·2	1650	0·31	0·2	0·51	12·8	8·3	21·1
0·25	1580	0·4	0·27	0·67	16·5	11·2	27·7
0·3	1520	0·47	0·33	0·80	19·4	13·6	33·0
0·4	1390	0·59	0·42	1·01	24·4	17·4	41·8
0·5	1310	0·67	0·46	1·13	27·7	19·0	46·7

It will be noticed that the conduction loss is from 40 to 60 per cent. greater than the radiation loss in each mixture. This applies, however, only to explosion vessels of the size used in these experiments. In much larger vessels the radiation loss per square centimetre may be greater than the conduction loss per square centimetre, for it increases with the size of the vessel,* whereas the conduction loss per unit area of wall surface is practically independent of the dimensions of the vessel.

It will be seen from the Tables that the 15 per cent. mixture has lost to the walls of the vessel 8·9 per cent. of its heat of combustion by the time it has attained its maximum pressure; of this 5·1 per cent. is due to conduction and 3·8 per cent. to radiation. The 12·4 per cent. mixture has lost at the same moment some 10 per cent. of its heat of combustion (5·5 per cent. by conduction and 4·5 per cent. by radiation). The loss at the moment of maximum pressure in the 9·7 per cent. mixture is much greater;† it amounts to about 18 per cent. of its heat of combustion, of which 11 per cent. is due to conduction and 7 per cent. to radiation.

Further information with regard to the heat lost up to the moment of maximum temperature ($\theta_{\max.}$) is set out in Table IV. It will be seen from this Table that the heat loss per square centimetre up to this moment ($H_{\max.}$) is proportional to the product of $\theta_{\max.}^{2.5}$ and the time of explosion (t_e), and that the proportion of the heat of combustion lost up to this moment

* See p. 308. It is estimated that in a vessel 70 cm. in diameter by 70 cm. in length, the radiation loss would be about the same as the conduction loss for mixtures at atmospheric density.

† This is due to its much longer explosion period. The time of explosion in the 9·7 per cent. mixture is 0·18 sec., whereas it is only 0·05 sec. and 0·08 sec. in the 15 per cent. and 12·4 per cent. mixtures respectively.

Table IV.—Heat Loss to Walls of Vessel up to Moment of Maximum Temperature.

Mixture.	Max. abs. temp. of gaseous mixture ($\theta_{\max.}$).	Time of explosion (t_e).	Heat loss in calories per sq. cm. up to max. temp. ($H_{\max.}$).	$\frac{H_{\max.}}{\theta_{\max.}^{2.5} \times t_e}$.	Proportion of heat of combustion of coal-gas lost to walls up to max. temp. ($H_{C. \max} = \frac{H_{\max.} \times 4380}{C}$).	$\frac{H_{C. \max.}}{\theta_{\max.}^{1.5} \times t_e}$.
per cent.						
15	2440	0.05	0.33	2.24×10^{-8}	0.089	1.47×10^{-5}
12.4	2050	0.08	0.31	2.08	0.10	1.36
9.7	1660	0.18	0.43	2.12	0.18	1.47
Mean values				2.15×10^{-8}	.	1.43×10^{-5}

($H_{C. \max.}$) is proportional to the product of $\theta_{\max.}^{1.5}$ and t_e . The experimental results indicate that $H_{\max.}$ and $H_{C. \max.}$ may be calculated for any mixture by means of the equations

$$H_{\max.} = 2.15 \times 10^{-8} \theta_{\max.}^{2.5} \times t_e$$

and

$$H_{C. \max.} = 1.43 \times 10^{-5} \theta_{\max.}^{1.5} \times t_e.$$

These equations, of course, hold only for coal-gas mixture contained in a vessel of the same size and shape as that used in these experiments and exploded at atmospheric density.*

The curves in fig. 4 and the figures in Table V show the rate of heat loss (radiation, conduction and total) in the various mixtures. It has been shown in a previous paper† that when the gaseous mixtures are exploded at atmospheric density the rate at which they lose heat by radiation per square centimetre of wall surface per second (\dot{R}) in the experimental vessel is approximately given by

$$\dot{R} = 1.75 \times 10^{-14} \theta^4,$$

where θ is the mean absolute temperature of the gaseous mixture. It was further shown that in a cylindrical vessel l cm. in diameter and l cm. in length that

$$\dot{R} = 0.32 \times 10^{-14} \theta^4 \sqrt{l}.$$

It has also been shown‡ that the rate of loss of heat by conduction per

* This is because that part of $H_{\max.}$ and $H_{C. \max.}$ which is due to radiation is dependent both upon the density and the volume of the gaseous mixture.

† 'Phil. Mag.,' January, 1920, p. 66.

‡ 'Phil. Mag.,' September, 1920, p. 326.

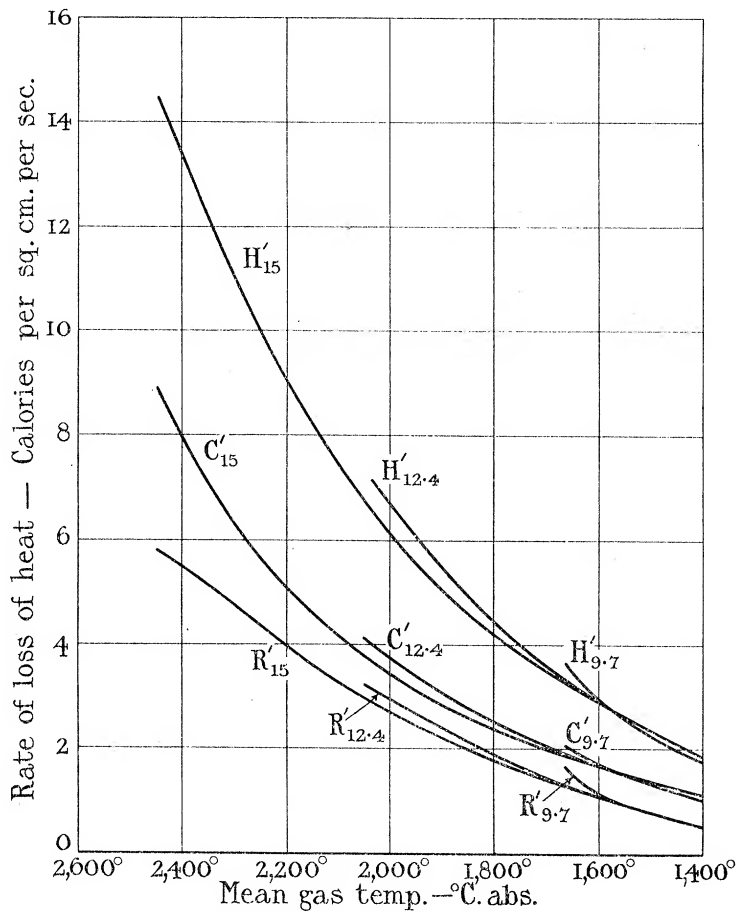


FIG. 4.—Rate of loss of heat in 15, 12.4, and 9.7 per cent. mixtures. H' curves, total heat-loss ; C' curves, loss by conduction ; R' curves, loss by radiation.

Table V.—Rate of Loss of Heat in 15 per cent., 12.4 per cent., and 9.7 per cent. Mixtures of Coal-Gas and Air.

Mean gas temperature (° C. abs.).	Rate of loss of heat. Calories per sq. cm. per sec.								
	15 per cent. mixture.			12.4 per cent. mixture.			9.7 per cent. mixture.		
	Conduction.	Radiation.	Total.	Conduction.	Radiation.	Total.	Conduction.	Radiation.	Total.
2440	8.7	5.8	14.5						
2400	7.9	5.4	13.3						
2200	5.0	3.9	8.9						
2050	3.8	2.9	6.7	4.1	3.2	7.3			
2000	3.4	2.7	6.1	3.7	2.9	6.6			
1800	2.4	1.8	4.2	2.5	1.9	4.4			
1660	1.9	1.4	3.3	1.9	1.4	3.3	2.1	1.6	3.7
1600	1.7	1.2	2.9	1.7	1.2	2.9	1.8	1.2	3.0
1400	1.2	0.7	1.9	1.2	0.7	1.9	1.1	0.7	1.8

square centimetre of wall surface per second (\dot{C}) is approximately given by

$$\dot{C} = 4 \times 10^{-13} (\theta - \theta_w)^4$$

for temperatures above 2000° C. abs. and by

$$\dot{C} = 7 \times 10^{-10} (\theta - \theta_w)^3$$

for temperatures below 2000° C. abs.; where $(\theta - \theta_w)$ is the difference between the temperature of the gaseous mixture and that of the walls of the explosion vessel. It is probable that \dot{C} is independent of the size of the vessel and the above formulæ, therefore, probably hold for a vessel of any dimensions.

The rate of total heat loss per square centimetre of wall surface per second (\dot{H}) in a cylindrical vessel l cm. by l cm., containing mixtures of coal-gas and air at atmospheric density is therefore given approximately by

$$\dot{H} = 4 \times 10^{-13} (\theta - \theta_w)^4 + 0.32 \times 10^{-14} \theta^4 \sqrt{l}$$

for temperatures above 2000° C. abs. and by

$$\dot{H} = 7 \times 10^{-10} (\theta - \theta_w)^3 + 0.32 \times 10^{-14} \theta^4 \sqrt{l}$$

for temperatures below 2000° C. abs.

Internal Energy of the Gaseous Mixtures.

From the experimental results described in the preceding section an estimate of the internal energy of the gaseous mixtures at various temperatures may be obtained. The internal energy at any moment is equal to the heat of combustion of the coal-gas originally in the vessel less the heat loss to the walls of the vessel up to that moment. The values of the internal energy of the different mixtures at various temperatures derived in this way are given in Tables VI, VII, and VIII.

The figures in column 4 of the Tables have been taken from the curves in figs. 1, 2, and 3. They give the total heat loss (*i.e.*, the radiation and the conduction losses) per square centimetre of wall surface when the gas temperatures have fallen to the values shown in column 2. The figures in column 5 represent the total heat loss over the entire surface of the vessel. They have been obtained by multiplying the figures in column 4 by 4380, which is the area in square centimetres of the interior surface of the explosion vessel. The figures in column 6 give the internal energy (reckoned from atmospheric temperature) of the gaseous mixtures in the explosion vessel at the various temperatures given in column 3. These values have been calculated by subtracting the total heat loss from the heat of combustion of the coal-gas. The volume of the gaseous mixture in the vessel, measured at

Table VI.—Internal Energy of 15 per cent. Mixture of Coal-Gas and Air after Explosion. Heat of Combustion of Coal-Gas in Vessel = 16,300 calories.

Composition of Mixture after Combustion $\left\{ \begin{array}{l} \text{N and O...71.5 per cent.} \\ \text{CO}_2 \text{ 8.5 } \text{ , ,} \\ \text{H}_2\text{O20.0 } \text{ , ,} \end{array} \right.$

Time after ignition (secs.).	Mean gas temperature (° C. abs.).	Mean gas temperature (° C.).	Heat loss calories per sq. cm. (H).	Total heat loss over whole surface of vessel = H × 4380 (calories).	Internal energy of gaseous mixture in vessel reckoned from atmospheric temperature = 16,300 - H × 4380 (calories).	Internal energy of gaseous mixture per gramme-molecule reckoned from 100° C. (calories).
0	—	15	0	0	(16,300)	(17,550)
0.05	2440 (max. temp.)	2170	0.33	1,450	14,850	15,950
0.06	2400	2130	0.52	2,280	14,020	15,050
0.1	2200	1930	0.97	4,250	12,050	12,900
0.15	2000	1730	1.34	5,870	10,430	11,100
0.22	1800	1530	1.66	7,280	9,020	9,570
0.3	1600	1330	1.96	8,600	7,700	8,100
0.42	1400	1130	2.27	10,000	6,300	6,650

Table VII.—Internal Energy of 12.4 per cent. Mixture of Coal-Gas and Air after Explosion. Heat of Combustion of Coal-Gas in Vessel = 13,500 calories.

Composition of Mixture after Combustion $\left\{ \begin{array}{l} \text{N and O...76.6 per cent.} \\ \text{CO}_2 \text{ 7.0 } \text{ , ,} \\ \text{H}_2\text{O16.4 } \text{ , ,} \end{array} \right.$

Time after ignition (secs.).	Mean gas temperature (° C. abs.).	Mean gas temperature (° C.).	Heat loss calories per sq. cm. (H).	Total heat loss over whole surface of vessel = H × 4380 (calories).	Internal energy of gaseous mixture in vessel reckoned from atmospheric temperature = 13,500 - H × 4380 (calories).	Internal energy of gaseous mixture per gramme-molecule reckoned from 100° C. (calories).
0	—	15	0	0	(13,500)	(14,320)
0.08	2050 (max. temp.)	1780	0.31	1,360	12,140	12,950
0.11	2000	1730	0.48	2,100	11,400	12,050
0.2	1800	1530	0.93	4,070	9,430	9,900
0.3	1600	1330	1.31	5,740	7,760	8,150
0.45	1400	1130	1.63	7,150	6,350	6,650

Table VIII.—Internal Energy of 9·7 per cent. Mixture of Coal-Gas and Air after Explosion. Heat of Combustion of Coal-Gas in Vessel = 10,600 calories.

Composition of Mixture after Combustion $\left\{ \begin{array}{l} \text{N and O} \dots 81\cdot6 \text{ per cent.} \\ \text{CO}_2 \dots\dots\dots 5\cdot5 \quad ,, \\ \text{H}_2\text{O} \dots\dots\dots 12\cdot9 \quad ,, \end{array} \right.$

Time after ignition (secs.).	Mean gas temperature (° C. abs.).	Mean gas temperature (° C.).	Heat loss calories per sq. cm. (H).	Total heat loss over whole surface of vessel = H × 4380 (calories).	Internal energy of gaseous mixture in vessel reckoned from atmospheric temperature = 10,600 – H × 4380 (calories).	Internal energy of gaseous mixture per gramme-molecule reckoned from 100° C. (calories).
0	—	15	0	0	(10,600)	(11,050)
0·18	1660 (max. temp.)	1390	0·43	1,880	8,720	9,050
0·24	1600	1330	0·61	2,670	7,930	8,200
0·31	1500	1230	0·82	3,600	7,000	7,200
0·4	1400	1130	0·98	4,300	6,300	6,450

normal temperature and pressure, is 21 litres, and the internal energy per gramme-molecule (taken as 22·25 litres) is therefore equal to the internal energy of the gaseous mixture in the vessel multiplied by $\frac{22\cdot25}{21(1-x)}$, where x is the contraction of volume* which takes place during combustion. The figures in column 7 are those in column 6 multiplied by this factor, less about 350 calories, which is the internal energy per gramme-molecule between atmospheric temperature and 100° C. The figures in column 7, therefore, give the internal energy of the gaseous mixtures per gramme-molecule reckoned from 100° C.

The data in these tables have been plotted in fig. 5. The curves show the internal energy (reckoned from 100° C.) per gramme-molecule of the different mixtures at various temperatures. The chain-dotted curves show the values of the internal energy of the various mixtures used in my experiments, as calculated from the specific heat values determined by Holborn and Henning. The dotted curve shows Clerk's values for a mixture which is of nearly the same composition as the 9·7 per cent. mixture used in these experiments.† Clerk's values and those of Holborn and Henning and mine are compared in Table IX.

It will be seen that Clerk's results and mine for the weak mixture in the later stages of cooling are very nearly the same, but the values of Holborn

* This is of the order of 3 per cent.

† The composition of Clerk's mixture is:—N and O, 83 per cent.; CO₂, 5 per cent.; H₂O, 12 per cent.

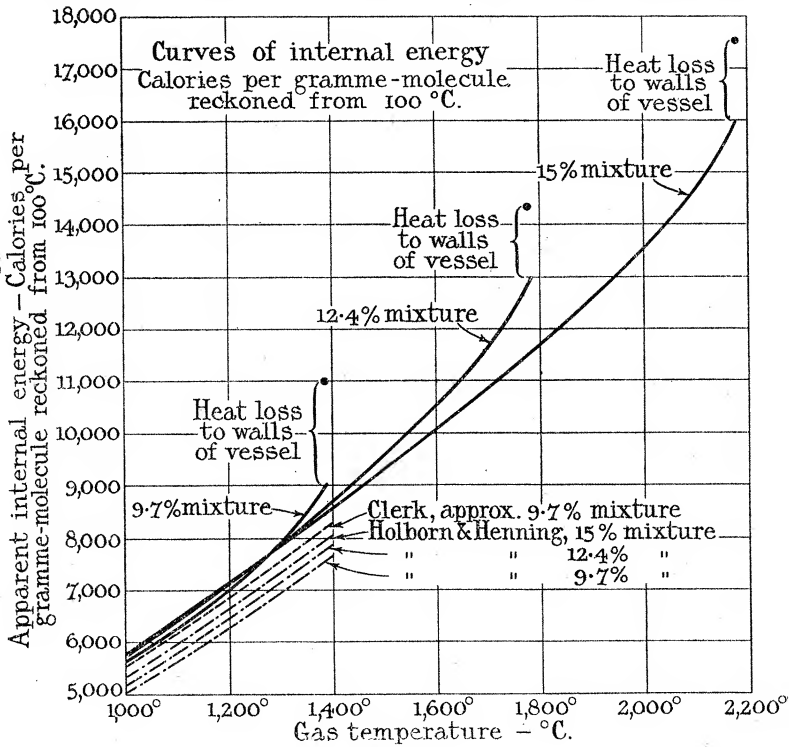


FIG. 5.

Table IX.—Internal Energy of the Gaseous Mixtures according to Holborn and Henning, Clerk, and the Explosion Experiments described in the present paper.

Mean gas temperature. (° C.)	Internal energy reckoned from 100° C.—calories per gramme-molecule.						
	15 per cent. mixture.		12.4 per cent. mixture.		9.7 per cent. mixture.		
	Explosion experiments.	Holborn and Henning.	Explosion experiments.	Holborn and Henning.	Explosion experiments.	Holborn and Henning.	Clerk.
2170*	16,000						
2000	13,600						
1800	11,700						
1780†	11,500	—	12,900				
1600	10,100	—	11,500				
1400	8,600	8,100	8,700	7,850			
1390‡	8,500	8,000	8,600	7,750	9,050	7,600	8,200
1200	7,200	6,700	7,200	6,500	7,050	6,300	6,900
1000	5,800	5,300	5,800	5,150	5,600	5,000	5,500

* (Max. temp., 15 per cent. mixture.) † (Max. temp., 12.4 per cent. mixture.)

‡ (Max. temp., 9.7 per cent. mixture.)

and Henning are considerably lower. The absolute values of the internal energy, as determined by my experiments, are subject to a possible error of some magnitude in that the conduction loss, having been determined in one position only, may not give a true average for the whole vessel. They cannot be used, therefore, to decide between Clerk's results and those of Holborn and Henning.* But the closeness between my results in the later stages of cooling and these results lends considerable confidence to the view that they show with a considerable degree of accuracy the variation in the internal energy values with temperature and time after ignition, and it is to a discussion of this that the remainder of the paper will be devoted.

The most noticeable feature of the internal energy curves is their rapid variation with temperature in the neighbourhood of the maximum temperatures and in the initial stages of cooling. It will be seen that the weaker mixtures in the initial stages of cooling possess a much greater apparent internal energy than the stronger mixtures when they have cooled to the same temperatures as the weaker mixtures have in this epoch—even though the stronger mixtures contain a larger proportion of CO_2 and steam than the weaker mixtures. This is also clearly shown by the curves in fig. 6,† which are the differentials of the internal energy curves in fig. 5 with respect to temperature. They show the rate of change of internal energy with temperature, or in other words, the instantaneous values of the volumetric heat (or rather of the *apparent* volumetric heat) of the various gaseous mixtures. In the case of the weaker mixtures the apparent volumetric heat values at maximum temperature and in the initial stages of cooling are very much greater than those of the stronger mixtures when they have cooled to the same temperatures as the weaker mixtures have in this epoch; indeed, in the neighbourhood of the maximum temperatures of the weaker mixtures the apparent volumetric heat of these mixtures is about three times as great as that of the stronger mixtures.

It is difficult to account for these results except in terms of continued combustion.‡ They cannot be explained in terms of the large temperature

* It is the general impression that the true values lie somewhere between Clerk's values and those of Holborn and Henning. (See 'First Report of the British Association Committee on Gaseous Explosions.')

† There is some uncertainty as to the exact values of the apparent volumetric heat values in the immediate neighbourhood of the maximum temperatures, and the curves in fig. 6 have accordingly not been continued to cut the dotted lines of maximum temperatures. They would appear to be between 20 and 30 calories per gramme-molecule at these temperatures.

‡ Hopkinson concluded from his experiments with platinum wires ('Roy. Soc. Proc.,' A, vol. 77, p. 409) that combustion once initiated in any part of the gaseous mixture was almost instantaneously completed. I am doubtful, however, whether the state of the gas

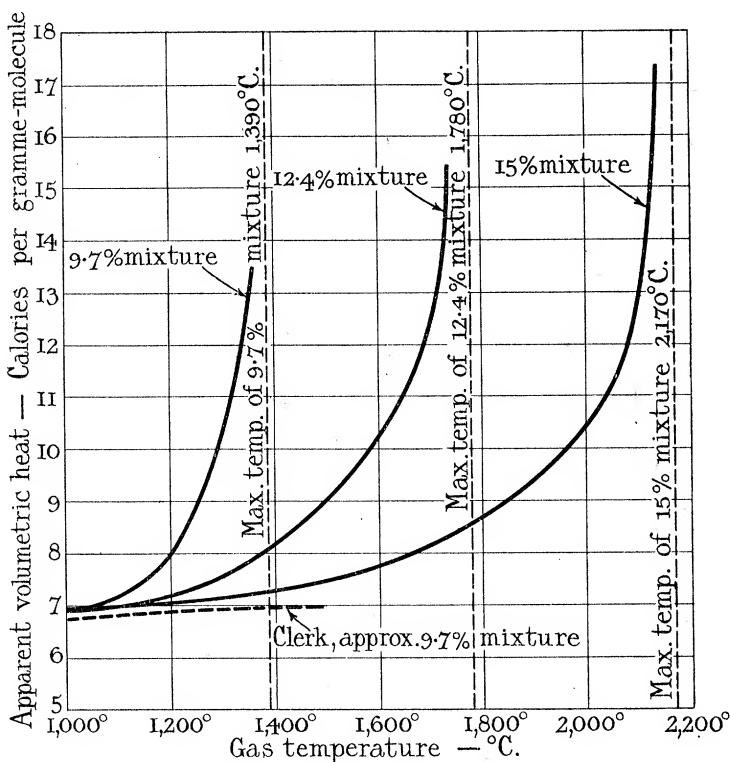


FIG. 6.—Volumetric heat of the various mixtures.

differences which exist in the gaseous mixtures at the moment of attainment of maximum temperature and the increase of the volumetric heat with temperature, for its rate of increase at these high temperatures is far too small to account to any appreciable extent for the results. Nor is it likely that they can be explained in terms of an excess of intra-molecular energy in this epoch; for it is highly probable that the rate of transfer of energy between the internal and the translational degrees of freedom of the molecules is extremely rapid at the high explosion temperatures.

Assuming then, as seems highly probable, that the apparent internal energy at maximum temperature and in the initial stages of cooling consists partly (and mainly) of thermal energy and partly of available chemical energy, an estimate of the amount of chemical energy in the gaseous mixtures in this epoch may be made from the curves. Such an estimate is obtained by subtracting from the apparent internal energy values of the weaker mixtures the internal energy values given by the curve for the strong mixture when near the wires was representative of that throughout the mass of the gas. Surface combustion probably speeded up the burning of the gaseous mixture in the immediate neighbourhood of the wires.

equilibrium has been attained, after making, of course, an allowance for the difference in composition of the mixtures. Estimates obtained in this way for the various mixtures at the moment of maximum temperature are given in Table X. The amount of heat lost to the walls of the explosion vessel up to this moment is also given in the Table.

Table X.—Distribution of Energy per Gramme-molecule at the Moment of Maximum Temperature.

Mixture.	Heat of combustion.	Internal thermal energy.	Available chemical energy.	Heat loss to walls of explosion vessel.
15 per cent.	17,600 100	14,200 81 per cent.	1,800 10 per cent.	1,600 9 per cent.
12·4 per cent. ...	14,350 100	11,200 78 per cent.	1,700 12 per cent.	14,500 10 per cent.
9·7 per cent. ...	11,050 100	8,000 72·5 per cent.	1,050 9·5 per cent.	2,000 18 per cent.

It will be seen from the Table that about 10 per cent. of the coal-gas originally in the vessel appears to be unburnt in each mixture at the moment of maximum temperature. Maximum temperature and pressure would therefore appear to be reached when about 90 per cent. of the coal-gas has been burnt. The proportion of the heat of combustion in the form of thermal energy at the moment of maximum temperature varies from about 80 per cent. in the 15 per cent. mixture to about 72 per cent. in the 9·7 per cent. mixture; and the heat loss to the walls up to this moment ranges from about 9 per cent. of the heat of combustion in the 15 per cent. mixture to about 18 per cent. in the case of the 9·7 per cent. mixture.

These results may be summarised in the form of an equation. Let

C be the heat of combustion of the coal-gas in the experimental vessel,
 $C_{\max.}$ be the proportion of the coal-gas unburnt at the moment of maximum temperature,

$E_{\theta, \theta_{\max.}}$ the internal thermal energy (reckoned from atmospheric temperature) of the gaseous mixture in the experimental vessel at the moment of maximum temperature,

and $H_{\max.}$ the heat loss per square centimetre of wall surface up to the moment of maximum temperature.

Then

$$C = E_{\theta, \theta_{\max.}} + C_{\max.} C + 4380 H_{\max.},$$

and therefore,

$$\begin{aligned} E_{\theta_e, \theta_{\max.}} &= 0.9C - 9.4 \times 10^{-5} \theta_{\max.}^{2.5} \times t_e \\ &= (0.9 - 1.43 \times 10^{-5} \theta_{\max.}^{1.5} \times t_e) C, \end{aligned}$$

since $C_{\max.} = 0.1$ approximately, $H_{\max.} = 2.15 \times 10^{-8} \theta_{\max.}^{2.5} \times t_e$

and $H_{C.\max.} = 1.43 \times 10^{-5} \theta_{\max.}^{1.5} \times t_e$.*

The internal (thermal) energy (reckoned from atmospheric temperature) per gramme-molecule is obtained by multiplying the values for $E_{\theta_e, \theta_{\max.}}$ calculated by means of the formulæ given above by the factor $\frac{22.25}{V_0(1-x)}$

where V_0 is the volume of the gaseous mixture before inflammation, measured at normal temperature and pressure, and x is the contraction of volume which takes place on combustion.

These formulæ are useful in that by means of them it is possible to calculate the internal (thermal) energy at the moment of maximum temperature from data which may be furnished by pressure-time curves. It should be pointed out that they are strictly applicable only to coal-gas and air mixtures which are—

(i) Contained in a vessel of the same shape and size as that used in these experiments and exploded at atmospheric density, because the radiation part of the heat loss, $H_{\max.}$, varies both with the size and shape of the containing vessel, and also with the density of the gaseous mixture; and

(ii) Of approximately the same chemical composition as the mixtures used in the experiments, so that the rate of combustion and time of explosion, t_e , are similar.

An examination of the volumetric heat curves in fig. 6 seems to indicate that combustion is proceeding in appreciable volume in the 15 per cent. mixture until it has cooled to about 1400° C. (that is for roughly 0.3 second after ignition, or 0.25 second after maximum pressure). After this temperature has been reached the shape of the volumetric heat curve indicates that the gaseous mixture has practically attained chemical equilibrium. In the 12.4 per cent. mixture, combustion seems to be going on until it has cooled to below 1200° C. (that is, about 0.4 second after ignition, or 0.3 second after maximum pressure); and, in the 9.7 per cent. mixture, some burning seems to be going on after it has cooled to below 1100° C. (that is, about 0.5 second after ignition, or 0.3 second after maximum pressure).

* See p. 308.

Summary.

In the first section of this paper heat-loss measurements by conduction and by radiation made during the explosion and subsequent cooling of mixtures of coal-gas and air of various strengths have been combined. The heat loss by conduction was found to be from 40 per cent. to 60 per cent. greater than the loss by radiation in the experimental vessel. In a vessel rather more than twice as large the radiation loss would have been about equal to the conduction loss, and in a still larger vessel it would have been greater. Formulæ have been built up by means of which the total heat loss up to the moment of maximum pressure, and the rate of heat loss at any temperature during cooling may be calculated from data which may be obtained from the pressure-time curves.

In the second section of the paper the heat-loss measurements have been applied to the estimation of the internal energy and the volumetric heat of the different mixtures at various temperatures after explosion. An examination of the internal energy and volumetric heat curves so obtained indicates that at the moment of maximum pressure about 10 per cent. of the heat of combustion of the coal-gas in each mixture has not been converted into thermal energy, and that after-burning continues for at least 0.25 second after maximum pressure has been attained.

It is believed that these results show that the energy of combustion of the coal-gas originally in the vessel is distributed at the moment of maximum temperature as follows:—

- (i) *Internal (thermal) energy*: From about 72 per cent. of the heat of combustion of the coal-gas in a 9.7 per cent. mixture to about 80 per cent. in a 15 per cent. mixture.
 - (ii) *Available chemical energy*: About 10 per cent. in each mixture.
 - (iii) *Heat loss to walls of vessel*: From about 10 per cent. in a 15 per cent. mixture to about 18 per cent. in a 9.7 per cent. mixture.
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