The Specific Heats of Air, Steam and Carbon Dioxide.
By W. D. Womersley, M.A., B.Sc., Demonstrator in Mechanism and Applied Mechanics in the University of Cambridge.

(Communicated by Sir Dugald Clerk, F.R.S. Received August 30,—Revised November 25, 1921.)

The late Prof. Bertram Hopkinson designed a recording calorimeter for explosions, of which a description has already been given.* It was hoped, by means of this calorimeter, to measure the apparent specific heats of the mixture of gases expanding in a gas-engine cylinder. A charge of coal-gas and air was exploded in a closed cast-iron vessel, the walls of which were lined with a continuous copper coil. The coil formed one arm of a Wheatstone's bridge, and thus, by the change in resistance of the coil, it was possible to measure the heat passed into the walls from the gas at any instant after an explosion. Hence, provided the heat liberated in the explosion was known, that remaining in the gas at any temperature, inferred from the pressure, could be estimated. The difficulty of accurately estimating the heat liberated by the burnt gas could not, however, for a long time be surmounted. It seemed that, when the coal-gas was mixed with air, there was a spontaneous time reaction between the two, which caused a discrepancy of something like 10 per cent in the volume of combustible gas, and a corresponding decrease in the actual amount of heat liberated at the time of the explosion. This difficulty was eventually overcome by mixing the combustible gas with either air or oxygen in a separate vessel some considerable time prior to charging the calorimeter.

The apparatus and calorimeter used by the author had many improvements over the original one described by Prof. Hopkinson, and, instead of using coal-gas of variable quality, and requiring extensive analysis and calorimetry, the less complex gases, hydrogen and carbon monoxide, were used, mixed with either air or oxygen.

At the time the experiments, the results of which are to be given, were initiated and carried out, the information available on the specific heats at high temperatures was obtained from the researches of Holborn and Austin, Holborn and Henning, Mallard and Le Châtelier, Langen and Clerk. Pier had published his results uncorrected, but Bjerrum's corrections to Pier's results had not arrived. The Committee on Gaseous Explosions, appointed by the British Association, have fully considered the results of the former

* 'Roy. Soc. Proc.,' A, vol. 79 (1907).
workers, and their conclusions are contained in the various reports issued. Several different methods of research have been used, but there is no great uniformity in the results obtained by the various workers.

The explosion method of determining specific heats has several disadvantages, the chief of which are:

1. At the time of maximum pressure, chemical and thermal equilibrium by no means exist in the hot gases. That is, the whole of the heat has not been liberated, and the temperature across the mass of gas is not uniform.

2. Since the calorimeter must have a certain number of small passages leading to and from it, for filling, indicating, sampling, etc., it follows that,
when the charge is exploded, a certain proportion of the gas is compressed into these spaces and does not burn. And thus it requires very careful gas analysis, both before and after the explosion, in order to make certain of the actual quantity of heat liberated.

The recording calorimeter allows the heat in the gas to be estimated at times considerably remote from that of maximum pressure, so that the chemical and thermal equilibrium will be more nearly attained.

The author's experiments were carried out with due regard to all the points mentioned. Analyses of the combustible mixture were made on samples from the mixing vessel before passing to the calorimeter, from the calorimeter before explosion, and from the calorimeter after explosion, and any experiment was rejected in which the gas quantities did not agree in all three of these analyses. About one hundred experiments of the present series were carried out, of which about half were with hydrogen and air, and the remaining quarters with carbon monoxide and air, and carbon monoxide and oxygen, respectively. In the calculations were finally used twenty-four of the hydrogen series, sixteen of the carbon monoxide and air, and twelve of the carbon monoxide and oxygen.

The results are shown in the curves of fig. 1, in which are plotted the heat contents above 100° C. of steam, air and carbon dioxide per gramme-molecule for temperatures ranging up to 2000° C. The actual range of the experiments is from 1000° to 2000° C., and the lower parts have been filled in from the researches of Swann and Holborn and Henning. The figures from which the curves are prepared are given in Table I, together with the values of the mean volumetric heats for temperature gaps of 100° C. The hydrogen experiments gave the figures for steam and air, and the accuracy is believed to be within 1 or 2 per cent. The carbon dioxide curves are deduced as the phenomenon of after-burning was encountered, and so may be open to criticism.

General Calculations.

The quantities of heat liberated in the combustion of hydrogen to steam, and carbon monoxide to carbon dioxide, have been taken from Ostwald's 'Lehrbuch der Allgemeinen Chemie,' vol. 2, and are based on the results of Andrews and Favre and Silbermann. The figures are as under:

Hydrogen to steam—67,840 calories per gramme-molecule. Carbon monoxide to carbon dioxide—67,200 calories per gramme-molecule.

The hydrogen was purchased from the British Oxygen Company. The carbon monoxide was prepared by the author, 20 litres at a time, from sulphuric and oxalic acids, the carbon dioxide formed being absorbed by caustic soda.
Table I.—Energy in Gases per Gramme-Molecule above 100° C., and Mean Volumetric Heat per Gramme-Molecule from 0° C. to t° C. calories.

| Temperature (°C.) | Air | Steam | Carbon dioxide |
|------------------|-----|-------|---------------|
|                  | Energy | Mean volumetric heat | Energy | Mean volumetric heat | Energy | Mean volumetric heat |
| 100              | 0     | 4.900 | 0             | 6.59   | 0             | 7.0 |
| 200              | 510   | 5.000 | 1,330         | 6.65   | 1,680         | 7.95 |
| 300              | 1,040 | 5.090 | 2,020         | 6.70   | 2,640         | 8.35 |
| 400              | 1,570 | 5.177 | 2,710         | 6.76   | 3,060         | 8.72 |
| 500              | 2,140 | 5.256 | 3,430         | 6.85   | 4,710         | 9.03 |
| 600              | 2,710 | 5.332 | 4,180         | 6.92   | 5,810         | 9.31 |
| 700              | 3,290 | 5.402 | 4,950         | 7.02   | 6,950         | 9.56 |
| 800              | 3,890 | 5.471 | 5,770         | 7.14   | 8,090         | 9.76 |
| 900              | 4,490 | 5.532 | 6,630         | 7.29   | 9,240         | 9.94 |
| 1,000            | 5,100 | 5.590 | 7,590         | 7.50   | 10,390        | 10.09 |
| 1,100            | 5,720 | 5.644 | 8,640         | 7.75   | 11,570        | 10.21 |
| 1,200            | 6,340 | 5.698 | 9,770         | 8.03   | 12,710        | 10.32 |
| 1,300            | 6,960 | 5.729 | 11,030        | 8.35   | 13,890        | 10.41 |
| 1,400            | 7,590 | 5.766 | 12,440        | 8.74   | 15,050        | 10.50 |
| 1,500            | 8,220 | 5.803 | 14,120        | 9.23   | 16,210        | 10.57 |
| 1,600            | 8,850 | 5.838 | 16,060        | 9.82   | 17,390        | 10.66 |
| 1,700            | 9,480 | 5.869 | 18,150        | 10.46  | 18,490        | 10.70 |
| 1,800            | 10,120| 5.900 | 20,350        | 11.07  | 19,630        | 10.72 |
| 1,900            | 10,780| 5.930 | 22,720        | 11.69  | 20,740        | 10.72 |

The quantity of gas burnt in an explosion was obtained from an analysis of the contents of the calorimeter after the explosion, together with the reduction of pressure caused by the chemical contraction, and, in the hydrogen experiments, the condensation of the steam. Analysis was also made of the mixture before admission to the calorimeter, and of the mixture actually in the calorimeter before explosion. These analyses all agreed. Hempel’s pipettes and burettes were used for all the gases except hydrogen. The hydrogen was absorbed in a palladium tube.

The temperature of the gas at any instant was obtained from the pressure record given by a Watson type diaphragm indicator and calculated according to the usual gas laws:—

\[ T_2 - T_1 = T_1 \left( \frac{p_2}{p_1^e} - 1 \right) \]

where \( T_1 \) is the initial absolute temperature at pressure \( p_1 \), \( T_2 \) is the absolute temperature at pressure \( p_2 \), \( e \) is the coefficient of chemical contraction in the gas reaction and is proportional to the volume of gas burnt;
for example: if 16 per cent. of either hydrogen or carbon monoxide are consumed

\[ e = 1 - \frac{0.16}{2} = 0.92. \]

Thus, by suitable calibration of the indicator, the mean temperature of the gas may be measured directly from the photographic film.

The galvanometer, measuring the change of resistance of the copper coil, was calibrated on each film by marking the deflection due to a known change in the resistance of the coil arm of the bridge. This calibration made unnecessary the measurement of either the main current or of the other resistances in the bridge. For the very small deflection of the galvanometer encountered, the deflection is proportional to the change in resistance of the coil.

Of the heat which passes into the coil, a certain amount is conducted through to the backing between the coil and the cast-iron walls of the vessel. This has been taken into account by the method given by Hopkinson in his paper on "Radiation in a Gaseous Explosion,"* in which the backing is assumed to be an infinite solid whose surface undergoes a definite change of temperature, and so the following relation is obtained:

\[
\frac{\text{Heat to backing at time } T}{\text{Heat to coil}} = \frac{2}{C} \sqrt{\left(\frac{kC}{\pi}\right)} \cdot \frac{1}{\theta_T} \int_0^T \frac{d\theta}{dt} \sqrt{[T-t]} \, dt,
\]

where \( k \) and \( C \) are the thermal conductivity and capacity respectively per unit volume of the backing, \( C \) is a constant, \( \theta_T \) is the temperature of the coil at time \( T \).

The temperature of the surface of the backing is assumed to be the mean temperature of the coil and is obtained from the galvanometer deflection. In order to find the constants, a balance of the heats is obtained at 1 second after ignition, and the heat unaccounted for is assumed to have passed through to the backing. The heat in the gas at 1 second in the case of the hydrogen experiments is taken from Holborn and Henning's results, as the temperature is in the neighbourhood of 500° C. From this the combined constant \( \frac{2}{C} \sqrt{\left(\frac{kC}{\pi}\right)} \) is obtained and the absolute value of the factors is not measured.

The heat which has passed to the backing at 1 second, calculated in this manner, is never more than 9 per cent. of the heat lost at that time by the gas, and contains the combined errors of all the measurements throughout the experiment.

* "Roy. Soc. Proc.," A, vol. 84 (1910).
In the case of the hydrogen experiments a mean of the values obtained for
\[ \frac{2}{C} \sqrt{\left( \frac{ke}{\pi} \right)} \] has been calculated and then used for the heat passed to the backing at any time in each experiment. A very considerable error in this heat is only a small proportion of the total heat loss, so that strict accuracy in this point is not very important. The mean value of the constant for the hydrogen experiments was found to be 0.0625. This value has had to be used in the carbon monoxide experiments for reasons to be given later.

The calorimeter was 12 inches internal diameter by 12 inches long. The teak backing was \( \frac{1}{2} \) inch thick. The coil consisted of copper strip of \( \frac{1}{4} \) inch by 1/16 inch section, weighing with the fixing screws 4171 grms. The specific heat of the copper was 0.093 and the resistance temperature coefficient 0.00428. The resistance of the coil at 0°C was 0.1202 ohms. The internal volume of the calorimeter was 18.5 litres and the internal area of surface 3935 sq. cm. The galvanometer calibrating resistance was 0.0148 ohms. The indicator gave a deflection of 1.31 inches for a rise in pressure of 100 lbs. per square inch.

Two representative films are given; fig. 2 for the hydrogen and fig. 3 for the carbon monoxide experiments.
The heat liberated in the explosion is obtained from the amount of hydrogen estimated by the analyses as having been burnt. From the photographic record the heat which has passed into the walls at any temperature, suitably increased by the heat which has gone to the backing, is obtained. Thus the difference between these two quantities of heat is that remaining in the gas at the associated temperature. This remaining quantity is reduced to calories per gramme-molecule of gas cooling, and in order to bring the various gases...
to the same basis for comparison, the heat necessary to raise the various constituents from the initial temperature of the experiment to 100° C. and convert the water to steam has been subtracted. Thus there is left the
amount of heat necessary to raise a gramme-molecule of gas, consisting of various proportions of steam and nitrogen, from 100° C. to temperatures ranging from 1000° C. to 2000° C. In order to allocate these quantities of heat, part to the steam and part to the nitrogen, it is necessary to adjust the volume of first the one and then the other of the constituents to an uniform amount throughout the series of experiments, and calculate the quantities of heat then contained by the mixture accordingly. This procedure gives two sets of heat contents. In the one the volume of steam is constant and the nitrogen varies, and in the other the volume of nitrogen is constant and the steam varies. Curves can then be drawn showing the relation between the volume of the variable constituent and the heat contents of the mixture at various temperatures. These curves are shown in figs. 4 and 5. The points obtained are seen to lie sensibly on series of straight lines for the various temperatures, and the slopes of the lines give the heat contents of the variable constituent for the appropriate temperature. The mean positions of the lines through the points were obtained in a mechanical manner in order to avoid the personal element.

The values of the mean volumetric heat between 1000° C. and 2000° C. were then calculated, and completed between 100° C. and 1000° C. from the researches of other workers. These curves are given for steam and nitrogen in fig. 6.
In this series the temperature at one second was about 950° C. As a first 
approximation Holborn and Henning's values for the heat in the gas at one 
second were used, and it was found that there was a very considerable 
balance of heat to be accounted for as having passed through to the backing; 
in fact, much more than could possibly be the case, so the value of $\frac{2}{C} \sqrt{\left(\frac{ke}{\pi}\right)}$ 
from the hydrogen experiments was used and an amount of heat left 
unaccounted for. This latter quantity was found to increase with the 
strength of mixture burnt. It was first thought that Holborn and Henning's 
values must be far too low, and hence the heat unaccounted for was assumed 
to be contained by the carbon dioxide. The heat in this gas was then deduced 
by using the heat in the air as obtained from the hydrogen experiments. It 
was found, however, that the heat in the carbon dioxide at any temperature 
showed a definite increase with the strength of mixture exploded, which 
would not seem actually to be possible.

Another explanation is, that combustion, even at 1 second after ignition, 
is still incomplete. The photographic records show much slower combustion 
with the carbon monoxide than with hydrogen. Also the galvanometer spot 
in the hydrogen experiments is in a state of vibration entirely absent with 
carbon monoxide, which seems to indicate actual flame contact with the walls 
in the case of hydrogen, whilst the carbon monoxide flame dies out some 
distance away. This will leave an unburnt gas layer near the walls, which 
may eventually burn as the pressure falls and allows the gas to expand into 
the open again.

The results for air and steam are about 7¼ per cent. higher than those of 
Holborn and Henning at 800° C., and it is reasonable to assume that their 
values for carbon dioxide are a similar amount too low. This figure has 
therefore been taken, the values of the mean volumetric heat between 
100° C. and 200° C. obtained from Swann's values, and a free curve drawn 
through the points and carried along to 1000° C. The heat in the carbon dioxide 
at 1 second has been deduced from this curve. The heat actually accounted 
for at 1 second has been taken as the heat actually liberated at that time. 
This heat is made up of that in the carbon dioxide and air, that in the coil 
and that passed through to the backing, calculated by using $\frac{2}{C} \sqrt{\left(\frac{ke}{\pi}\right)}$ from 
the hydrogen experiments. The balance between the quantity of heat 
accounted for and that eventually liberated has been considered as still latent 
in the unburnt gas layer in contact with the walls. The heat accounted for 
at one second has been used to determine the heat left in the mixed gases at
times previous to 1 second. The heat in the air from the hydrogen experiments has been subtracted from this remainder, and thus the heat in the carbon dioxide should be left. The latter quantities are converted to calories per gramme-molecule above 100°C, and the average of the two

series, carbon monoxide and air and carbon monoxide and oxygen, are shown in fig. 7. The values of the mean volumetric heat are shown in fig. 8.

It is evident that if a certain amount of carbon monoxide is still unburnt at the expiration of one second, even more will be unburnt at times earlier
than this, and thus the amount of heat left in the carbon dioxide will be too large by an increasing amount, as the time from ignition is shorter. As there seems to be no method of estimating the amount of unburnt gas at any earlier period the volumetric heat curve has been continued in a free manner up to 2000° C., and the heat actually in the carbon dioxide deduced from this. It will be noticed that the carbon monoxide—oxygen experiments give results somewhat higher than the carbon monoxide—air experiments. The variation is about 2 per cent. at 1000° C., 6 per cent. at 1500° C., and gradually

Fig 8
decreases to 1 per cent. at 2000° C. In the former experiments the products of combustion are carbon dioxide and oxygen, and in the latter, carbon dioxide and nitrogen. The difference represents a very small quantity of heat in the actual volume of carbon dioxide present after explosion and is possibly within the limits of error of the experiments. Otherwise a small difference in the heat contents of the oxygen and nitrogen would bring the curves together, if that in the oxygen were the larger. Up to 800° C., however, Holborn and Henning found the reverse to be the case. It was also noticed that there was a greater proportion of unburnt carbon monoxide in the oxygen experiments than in those with air, and the temperatures at one second are considerably lower.

A mean of the volumetric heats for the two curves has been obtained. This mean curve lies along the free curve up to 1200° C., and beyond this temperature rises above the free curve at an uniform rate to about 1700° C. Above 1700° C. the rate of separation of the curves makes a further increase. It is thought that the difference between the curves from 1200° to 1700° C. will solely represent an increasing amount of unburnt gas. At higher temperatures the difference will include any dissociation, and also the lack of thermal equilibrium, as the higher temperatures are very close to the point of maximum pressure.

It is clearly recognised that the whole of the figures for carbon dioxide are deduced, but it is thought that the basis is sufficiently sound, at least from 1000° to 1200° C., to warrant the acceptance of the results to within 2 per cent. Above 1200° C. the figures are obtained from a free curve which has no checking point at the higher temperature end, and so may be considerably in error. It is thought, however, that they are likely to be more correct than those of Langen, or of Mallard and Le Châtelier, which have been taken up to the present, as it would seem that their experiments also must contain this unburnt gas, for which no correction seems to have been made.

The author would like to dedicate this work to the late Prof. Bertram Hopkinson, as the idea of the calorimeter was his, and he first suggested the line of research to the author. The work represented in this paper was carried out, after the death of Prof. Hopkinson, in the Engineering Laboratories of Cambridge University, and the author would like to thank Prof. Inglis and Mr. C. G. Lamb for their kindness in placing the resources of the laboratories at his disposal.
APPENDIX I.

The Effect of the State of the Walls of the Containing Vessel on the Rate of Heat Flow in a Gaseous Explosion.

Measurements on the radiation from the gas to the walls of the containing vessel under different conditions were made by Mr. W. T. David. They are described in his paper, "Radiation in a Gaseous Explosion."* The author carried out a series of experiments with the Hopkinson calorimeter, to find the total heat passed to the walls after an explosion, first with the walls polished, and then blackened. The polished surface of the copper coil was obtained by the use of petrol, bath brick and rags, chiefly the latter, and rubbing was continued until no further change was visible to the naked eye. The other surface was obtained by painting over the coil with vegetable

* 'Roy. Soc. Proc.,' A, vol. 211 (1910).
black, the medium being petrol, and the walls were a dull black when dry. Coal gas was used in the combustible mixture, and five experiments, under each of the different conditions, were made. The same mixture strength was used throughout, viz., 12·35 per cent. of coal gas by volume.

The cooling curve and the total heat loss to the walls are shown in fig. 9. The maximum temperatures reached are 2123° and 2089° C. absolute respectively, giving a difference of 34° C. At the end of 1 second the gases have cooled to 918° and 859° C. absolute, a difference at this point of 59° C. It may be noted that the heat lost to the walls in the two cases, when cooling has proceeded to the same temperature, is sensibly the same. To convert the heat lost to the walls to calories per square centimetre per gramme-molecule of gas cooling, the figures on the curve should be multiplied by the factor 0·000338.

At 1 second, the heat passed to the walls per square centimetre per gramme-molecule is 2·675 and 2·556 calories respectively.
David found that, at the end of 1 second, in a 13 per cent. mixture, the heat received in the walls by radiation was about 0.81 calories, with walls and bolometer black. This, taken in conjunction with the above figures, show that 30 per cent. of the heat lost by the gas at 1 second is radiated to the walls, and the remaining 70 per cent. passes by conduction, etc.

Fig. 10 shows the rate of heat flow to the walls at various times during the cooling, and it will be seen that during the first half second the rate is much greater with the walls black than when they are polished. After this time the rates seem to be practically the same in the two cases. The rate of heat flow at various temperatures is also shown in fig. 10, and indicates a 16 per cent. higher rate throughout with the blackened walls.

Plotted logarithmically, the temperature curves from fig. 10 give the following relations between the rate of heat flow and the difference of mean gas temperature and walls:

for black walls
\[
\frac{dH}{dt} = 1.766 \times 10^{-6} \times T^{2.054},
\]

for polished walls
\[
\frac{dH}{dt} = 1.462 \times 10^{-6} \times T^{2.059},
\]

where \( T \) is the difference between the average temperature of the walls and the mean temperature of the gas,

\( \frac{dH}{dt} \) is the rate of heat flow to the walls in calories per square centi-metre per second per gramme-molecule of gas cooling.