THE SPECIFIC HEAT OF GASES AT HIGH TEMPERATURES

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[Plate 1]

1. Introduction

For many years work has been in progress in the Engineering Department of the National Physical Laboratory on problems involving the explosion of gaseous mixtures in a closed vessel or bomb (Fenning 1924, 1925, 1926; Fenning and Tizard 1927). The experience gained and the technique developed were considered to warrant a new attack being made on the measurement of the specific heats of gases at high temperatures, particularly of those gases which comprise the working substance of the internal combustion engine. The work was therefore put in hand and carried out for the Department of Scientific and Industrial Research.

At the time the investigation was started a considerable amount of data, based on explosion experiments, was available, and this was being supplemented by values of the specific heat obtained from the analysis of the band spectra of the gases concerned. Activity in this latter field has continued and values are now available for a considerable number of gases over a wide temperature range as will be seen from a summary by Lewis and von Elbe (1935 *a*) published about three years ago.

For the direct determination of the specific heat of gases at very high temperatures there seem to be no practicable alternatives to the explosion method. This method has been subjected to adverse criticism, but when it is realized that experiments involving temperatures of the order of 2000 to 2800° C are unlikely to be free from considerable difficulties, it must be admitted that the explosion method has the merit of comparative simplicity, so far as the greater part of the experimental technique is concerned. Much of the adverse criticism of the explosion method has been discussed in a paper by Lewis and von Elbe (1934 *d*), who conclude that the method is satisfactory provided certain conditions are observed and due allowance is made for the temperature gradient in the gaseous mixture at the maximum explosion pressure. If a direct measurement of the heat loss to the walls of the explosion vessel can be avoided, the requisite experimental readings are less difficult to obtain than they are to interpret, for the analysis of the results requires, first, a knowledge of the extent to which all possible chemical reactions can proceed under the temperature and pressure conditions reached in the explosion; secondly, a method for correcting for the temperature gradient that pertains

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to the gaseous contents of the bomb under those conditions; thirdly, accurate data as to the heat of formation of the gases concerned; and lastly, a knowledge of the departure of gas mixtures from the ideal gas conception.

In the present investigation a direct measurement of the heat loss to the explosion vessel walls was avoided and the analysis of the results was helped by the publications of other investigators, particularly those of Lewis and von Elbe.

Thus the investigators named give in their published summary (Lewis and von Elbe 1935*a*)—to which allusion has already been made—the dissociation or equilibrium constants for a number of gases. The sources from which these constants have been obtained are indicated, and it will be found that, although one or two are based entirely on spectroscopic data, others depend on free-energy values derived from such data and on heats of formation obtained from thermal measurements. For ease of application, the values given by Lewis and von Elbe have been expressed in the form of equations which represent them fairly closely over the temperature range 2000 to 3000° C (abs.). These equations, which were developed for the temperature range specified but have, on occasions, been used beyond it, have the form:

$$\text{(i)}\quad \log\frac{(P_{CO})^2\times P_{O_2}}{(P_{CO_2})^2}=8{\cdot}593-\frac{28{,}600}{T},$$

$$\text{(ii)}\quad \log\frac{(P_{H_2})^2\times P_{O_2}}{(P_{H_2O})^2}=6{\cdot}18-\frac{26{,}400}{T},$$

$$\text{(iii)}\quad \log\frac{P_{CO}\times P_{H_2O}}{P_{CO_2}\times P_{H_2}}=1{\cdot}2065-\frac{1100}{T},$$

$$\text{(iv)}\quad \log\frac{(P_{NO})^2}{P_{N_2}\times P_{O_2}}=1{\cdot}348-\frac{9475}{T},$$

$$\text{(v)}\quad \log\frac{(P_{OH})^2\times P_{H_2}}{(P_{H_2O})^2}=7{\cdot}56-\frac{28{,}670}{T},$$

$$\text{(vi)}\quad \log\frac{(P_H)^2}{P_{H_2}}=6{\cdot}37-\frac{23{,}820}{T},$$

$$\text{(vii)}\quad \log\frac{(P_O)^2}{P_{O_2}}=7{\cdot}021-\frac{26{,}640}{T},$$

$$\text{(viii)}\quad \log\frac{(P_N)^2}{P_{N_2}}=7{\cdot}080-\frac{37{,}920}{T},$$

where T is the temperature in ° C abs. and P_{CO}, P_{H_2}, etc. represent the partial pressure in atmospheres of the gas denoted by the suffix.

As to heats of formation, the values that have been used in the analysis of the present experiments are shown in the chemical equations given hereunder. The numerical values relate to constant volume conditions and to an initial and final temperature of

100° C, since the initial temperature in the explosion experiments approximated closely to that figure:

$$\begin{aligned} CO+\tfrac{1}{2}O_2 &\rightleftharpoons CO_2+67{,}390, \\ H_2+\tfrac{1}{2}O_2 &\rightleftharpoons H_2O\ (\text{gas})+57{,}660, \\ NO &\rightleftharpoons \tfrac{1}{2}N_2+\tfrac{1}{2}O_2+21{,}540, \\ OH+\tfrac{1}{2}H_2 &\rightleftharpoons H_2O+63{,}550, \\ 2H &\rightleftharpoons H_2+103{,}220, \\ 2O &\rightleftharpoons O_2+117{,}660, \\ 2N &\rightleftharpoons N_2+168{,}370, \\ N_2O &\rightleftharpoons N_2+\tfrac{1}{2}O_2+20{,}030. \end{aligned}$$

The heats of formation of carbon dioxide and water vapour are now fairly well established. Recent determinations of both these gases have been made by Rossini (1931 *a*, *b*, *c*), and his value for carbon dioxide has been substantially confirmed by Awbery and Griffiths (1933) and by Fenning and Cotton (1933). The pairs of investigators, just mentioned, are also each responsible for a recent value of the heat of formation of nitrous oxide. The heat of formation of nitric oxide is less well founded—the value taken being more or less a mean of values which differ considerably. In fact the work of Briner, Boner and Rothen (1926) indicates a higher value for the heat of formation of this gas and a much greater degree of dissociation than the values given above.

The heat of formation of hydrogen from atomic hydrogen is based on spectroscopic and calorimetric determinations, whereas the heat resulting from the formation of water vapour from OH and hydrogen is derived from explosion experiments by Lewis and von Elbe (1935 *b*). The heats of formation of oxygen and nitrogen have a spectroscopic basis.

With regard to the compressibility characteristics of the various gas mixtures both before and after explosion, it was considered reasonably safe to assume that under the high temperatures reached in the explosion the perfect gas state was attained. Direct experimental determinations could, however, be made in regard to the unburnt mixture at the charging pressure and temperature and this was, in fact, done. The method and apparatus are described in the Supplement.

Reference has already been made to determinations of specific heat based on spectroscopic data. Workers in this field are confident in the accuracy of their results so far as the diatomic gases are concerned and place considerable reliance on the values obtained for some of the triatomic gases. It is, therefore, of great interest to compare these "spectroscopic values" with those obtained in the present investigation and, as this has been done, it is necessary to give the source of the spectroscopic values that have been used. During the last few years Giauque (1930 *a*, *b*; Giauque and Overstreet 1932; Clayton and Giauque 1932), Johnston and their co-workers (Johnston and

Chapman 1933; Johnston and Walker 1933 *a*, *b*, 1935; Lewis and von Elbe 1933 *a*, *b*; Johnston and Dawson 1933; Giauque and Clayton 1933; Gordon 1934; Johnston and Davis 1934; Davis and Johnston 1934; Kassel 1934) have published their spectroscopic determinations of the molecular heat at *constant pressure* of such gases as hydrogen (Davis and Johnston 1934), carbon monoxide (Johnston and Davis 1934), nitrogen (Johnston and Davis 1934), oxygen (Johnston and Walker 1935), nitric oxide (Johnston and Chapman 1933), OH (Johnston and Dawson 1933), carbon dioxide (Kassel 1934), nitrous oxide (Kassel 1934) and water vapour (Gordon 1934), the temperatures extending in many cases up to 5000° C (abs.). From these published data *mean* molecular heats at *constant volume* have been deduced for the purpose of the present investigation (taking $R = 1{\cdot}987$ cal./g.-mol.) and the values obtained are given in Table I. A comparison of these values with those deduced from heat capacities given in Lewis and von Elbe's (1935 *a*) summary shows substantial agreement except in the case of oxygen, where the discrepancy is due to divergences in the allowances made for the $^1\Delta$ level of that gas (Lewis and von Elbe 1933 *b*; Johnston and Walker 1935). The values of the molecular heat of oxygen published by Johnston and Walker (1933 *a*) included no allowance for the energy due to the $^1\Delta$ level. Explosion experiments by Lewis and von Elbe (1933 *b*) led to their suggesting the existence of this level and computing the magnitude of its contribution, and this was followed by a revision by Johnston and Walker (1935) of their previous figures. The latter were increased by approximately 0·15, 0·30, 0·42 and 0·50 cal./° C at 2000, 2500, 3000 and 3500° C (abs.) respectively—to take full account of the level in question—and it is on these amended figures that the molecular heats of oxygen, given in Table I, are based.

2. Apparatus

(*a*) *Explosion vessel.* The explosion vessel, which was designed specifically for this investigation, is shown in section in fig. 1, and a photograph of the top half is reproduced in fig. 3, Plate 1. It is a hollow steel sphere of 12 in. (30 cm.) internal diameter and is made up in halves connected together by means of a flanged joint. The inside surface is coated with chromium and originally had a very high polish. During some of the preliminary series of experiments, however, the original polish was permanently diminished by the temporary application of a coating for varying the surface condition, but in spite of this the surface still showed good reflecting properties.

The manometer, inlet and outlet valves, windows and spark electrodes are all fitted to the lower half of the vessel so that the upper half can be removed without disturbing any of these fittings. The explosion vessel is surrounded by a gun-metal casing and the intervening space forms a "jacket" which can be supplied with steam, at a pressure slightly above the atmosphere, from an adjacent gas-fired boiler. The temperature of the explosion vessel—from which the initial temperature of its gaseous contents is inferred—was usually determined from the readings of two thermocouples inserted in holes drilled in the upper and lower halves of the vessel respectively, and these temperatures were checked from measurements of the steam pressure in the jacket. The agreement proved to be so close that eventually steam-pressure measurements were relied upon exclusively, a water U-tube being used for indicating the difference between the pressure of the steam and that of the atmosphere.

As will be seen from fig. 1, a half-millimetre spark gap, for the ignition of the charge, is situated at the centre of the vessel, the electrodes consisting of stainless steel rods. A secondary gap, located in the recording camera, enabled the passage of the spark to be recorded on the pressure-time diagram without appreciable lag.

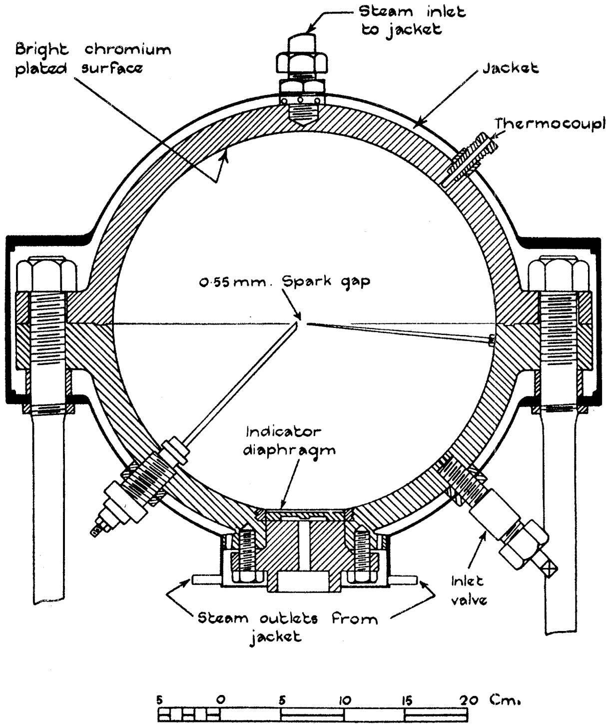

FIG. 1. Sketch of explosion vessel.

(*b*) *The cage.* It was considered worth while to develop some method for determining the *order of magnitude* of the loss of heat which occurs between the passage of the igniting spark and the attainment of the maximum explosion pressure.

The device employed consisted of a cage-like structure which, when inserted in the explosion vessel, was computed to increase its surface-volume ratio by about 56 %. At a somewhat later date this was supplemented by a dummy electrode so as to provide a somewhat similar increase in the surface of the electrodes.

The cage, which is illustrated in fig. 2 and by the photograph in fig. 3, Plate 1, consists of a set of interconnected steel fins, which are nickel plated on copper and polished. The fins taper towards the explosion vessel wall and are separated from it by a gap of about $1\frac{1}{2}$ mm. in order to avoid incomplete combustion due to the juxtaposition of cooling surfaces.

Explosion experiments carried out on the same mixture both with and without the cage gave cooling curves which indicated that the effect of the cage was to increase the surface-volume ratio by about 50 %, and this figure was accepted in place of the computed increase of 56 %.

The drop in the maximum explosion temperature due to the insertion of the cage cannot be taken as a measure of the heat loss due to a 50 % increase of the wall surface, for allowances have to be made for (i) the cage surface being enveloped or partially enveloped in flame for an appreciable time before the attainment of maximum temperature, (ii) the lowering of the maximum temperature itself, and (iii) changes in the degree of dissociation due to the lowering of that temperature. A review of the method

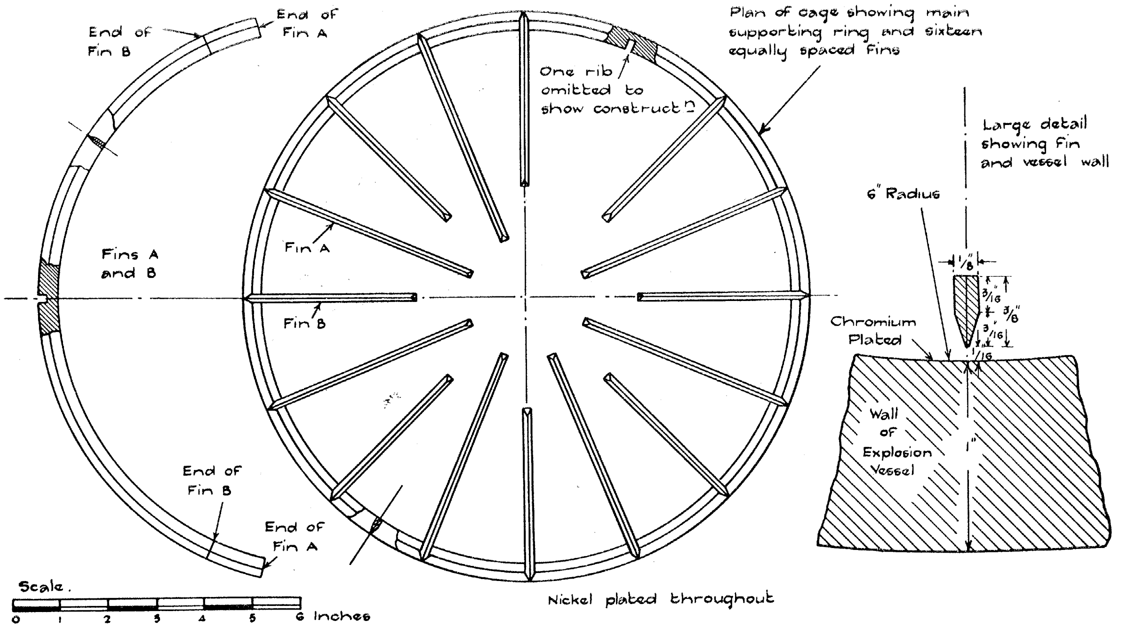

FIG. 2. Internal cage to provide additional cooling surface for explosion vessel.

and its defects, and of the corrections applied is given later (p. 182). It leads to a lower estimate of the effectiveness of the method than experience seems to warrant.

(*c*) *The manometer and its calibration.* The manometer used for obtaining a pressure-time record of the explosion is of the type that has been developed in the Engineering Department of the N.P.L. in connexion with previous researches involving gaseous explosions. Fig. 4 is a sectional drawing of the instrument: it shows the particular form of diaphragm adopted and the way in which it is protected by a mica and sheet metal covering from temperature change during the early portion of the pressure record. The deflexion of the diaphragm is transmitted to a light steel lever fitted with a stainless steel concave mirror of about 1 m. radius of curvature. The resulting magnification is about 1300 to 1 and the maximum deflexion of the diaphragm is less than 0·05 mm. As will be seen from fig. 1, the face of the diaphragm is level with the inside surface of the explosion vessel, and an extension of the main steam jacket envelopes the diaphragm-portion of the manometer.

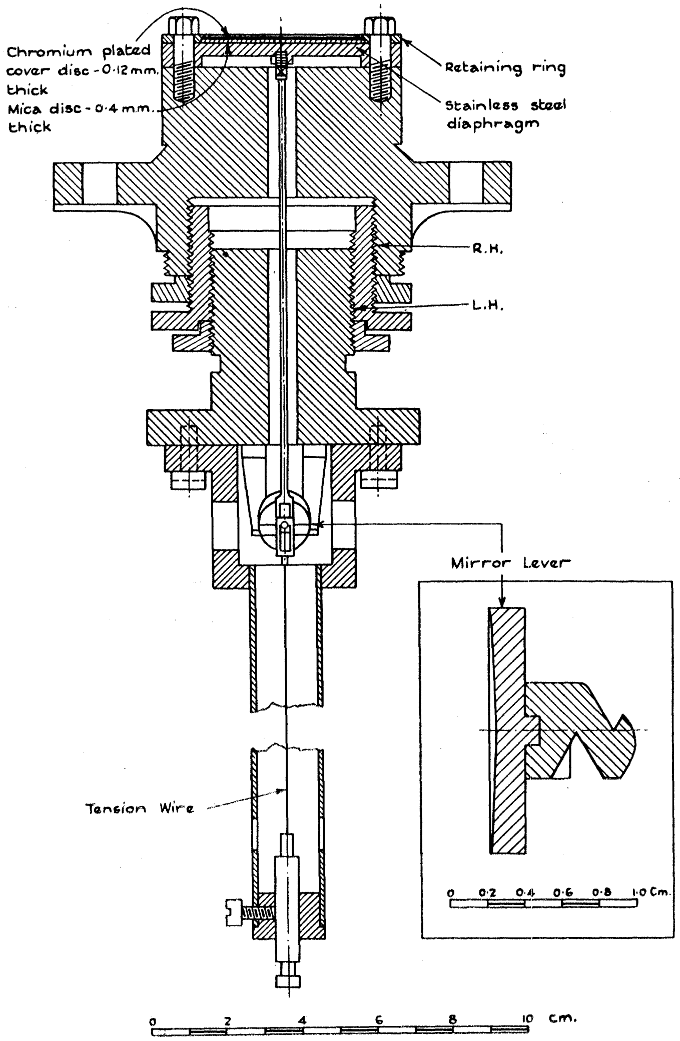

FIG. 4. Sketch of manometer for explosion vessel.

A full description of an earlier pattern of the manometer and its recording "camera" is given in an earlier paper (Fenning 1924), but this makes no reference to a device which has since been added for eliminating the effects of the atmospheric expansion and contraction of the sensitized paper on which the pressure-time diagram is recorded. The device consists of a rigid bar carrying two needle points at a known distance apart. The bar itself is carried by an arm which is hinged to one side of the camera box and is normally retained by a spring catch in position 1 (see fig. 5). Immediately after an explosion record has been taken, the bar is swung into position and pressed on to the sensitized paper enveloping the drum. The distance between the small perforations thus made can be readily measured by a travelling microscope and the necessary allowance made for any departure from the standard distance. No standard of reference is needed in the direction of the time axis, since arrangements are made to bring a tuning-fork into action about half a second after the firing of the charge. The tuning-fork intercepts the light falling on to the manometer mirror and so converts the cooling curve into a broken line which forms a time scale (see fig. 18, Plate 1).

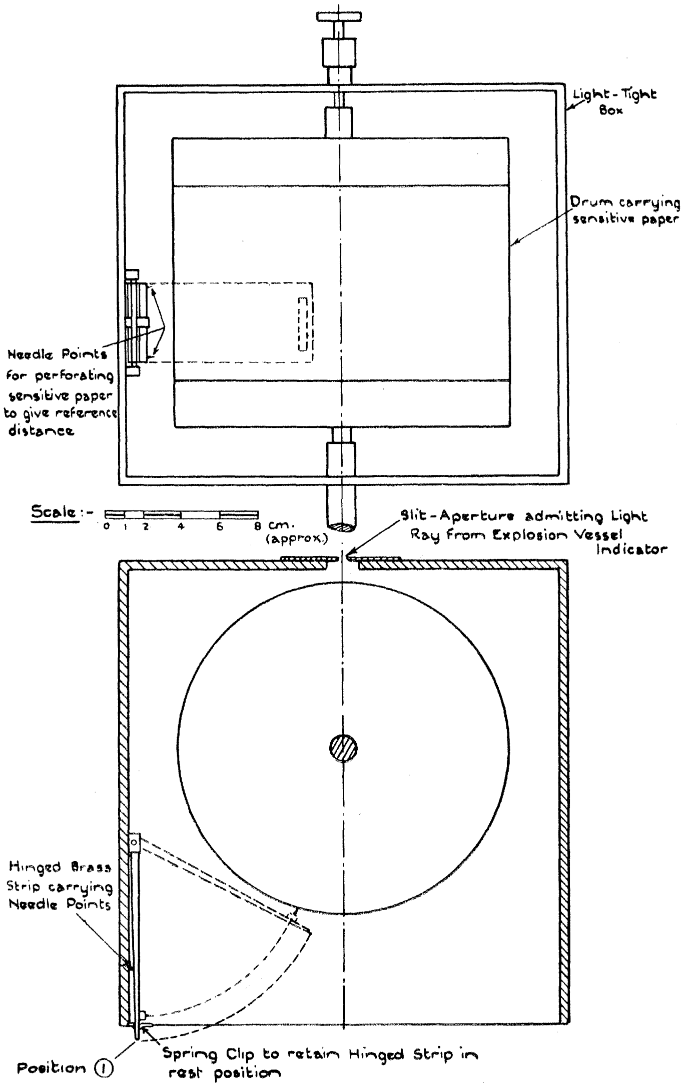

FIG. 5. Sketch of arrangement to obtain reference distance on explosion vessel pressure-time records.

The calibration of the manometer is an important factor. Calibrations in which the load is applied as rapidly as in the normal explosion seem to be desirable, but their interpretation is by no means easy. Following more or less the example of Pier (1909), the explosion vessel was designed so that a small ring encircling the manometer diaphragm could be removed and its place taken by a cap of comparatively small capacity connected directly to a steel bottle containing air at the required loading pressure (see fig. 6). By a quick opening of the valve between the bottle and the cap, a rapid loading of known intensity could be applied to the diaphragm and the resulting displacement of the light spot recorded simultaneously on a time base as in the normal explosion record. It was found, however, that the photographic records of these quick-loading calibrations could not be interpreted with precision, for there was no means of knowing *the exact time* at which the pressure in the cap was equal to the measured pressure in the bottle. In other words, it was impossible to say whether the final portion of the pressure-rise curve was due to pressure variations or to some creep effect. To assume that the pressure had ceased to rise when the displacement of the light spot had reached a maximum would be equivalent to calibrating the manometer against itself.

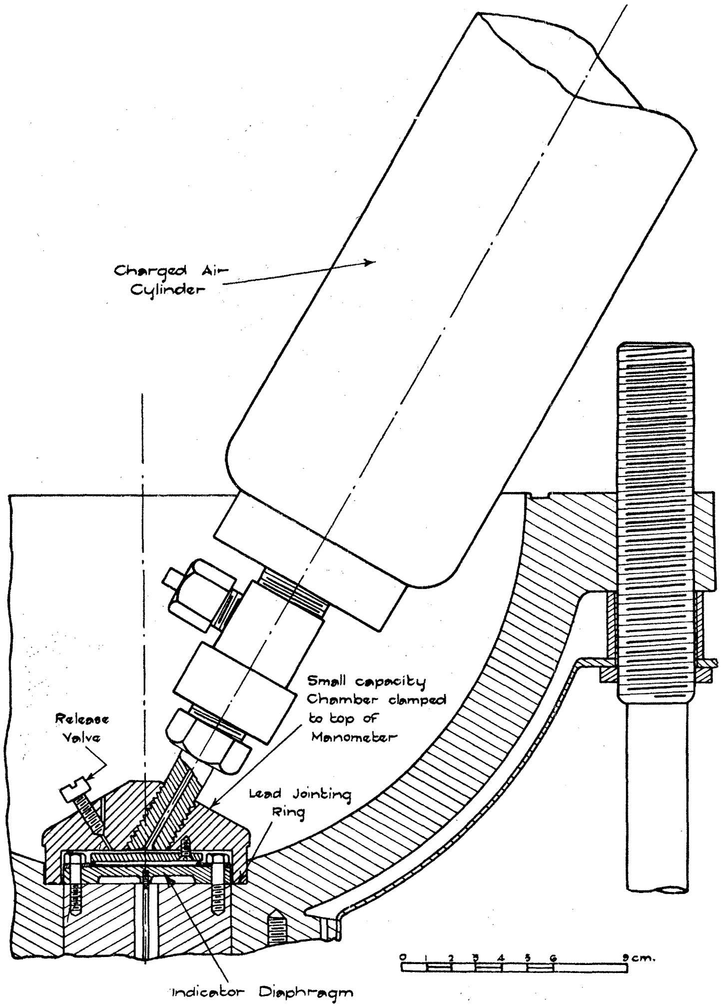

FIG. 6. Early form of apparatus used for dynamic calibration of manometer.

Various methods were tried for solving the difficulty that had arisen in ascertaining when the pressure in the cap was equal to that in the bottle. In the final scheme the cap was filled with water and a submerged orifice was used to control the rate of loading and make it largely independent of the rate of opening of the valve. Orifices of various sizes were formed in standard types of disk, and the face of each disk was lapped so as to make a water-tight joint with the seating on which it rested. The precaution of using a loose disk was taken in order to avoid the possibility of the pressure below the disk momentarily exceeding that above it. The arrangement is shown in fig. 7.

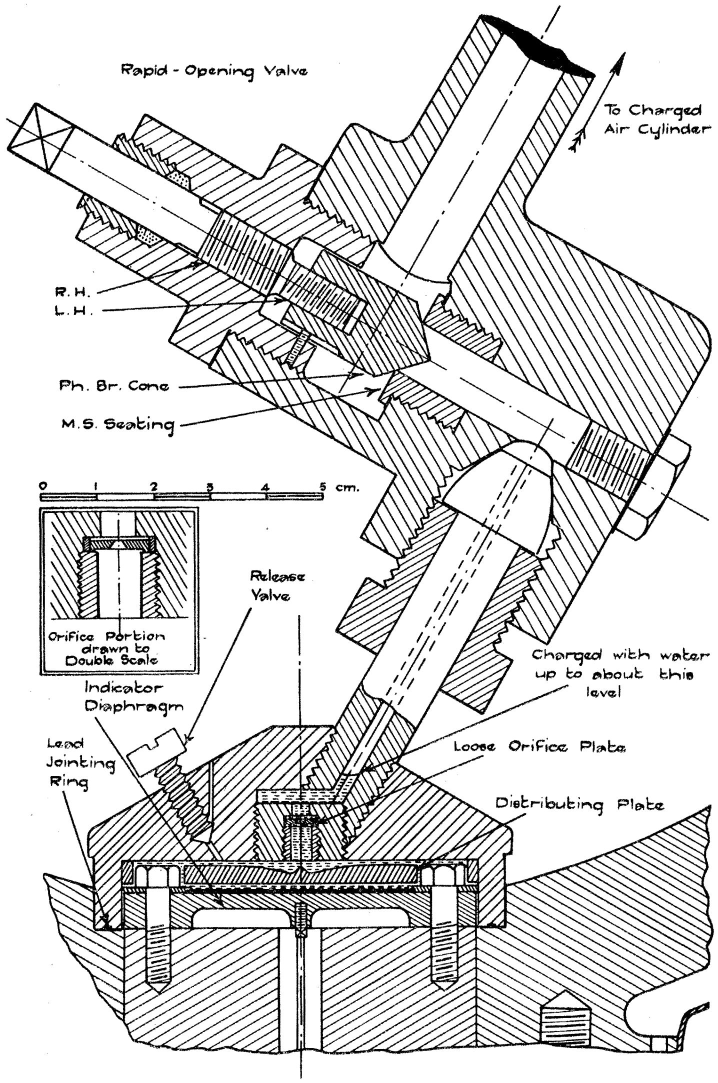

FIG. 7. Final form of apparatus for dynamic calibration of manometer.

In analysing the calibration records given by this apparatus it was assumed that, during the later stages of the pressure rise, the pressure on one side of the orifice was that recorded by the manometer, whereas the pressure on the other side was equal to that in the air bottle. From the slope of the pressure-time curve when the pressure was within say 5, 10, 15 lb. per sq. in. of the maximum, estimates could be formed of the time that should be taken for the pressure to equalize on the two sides of the orifice and hence of the time at which the pressure in the cap should equal that in the bottle. The analysis was facilitated by magnifying the original records some tenfold.

The various series of dynamic calibrations occupied a considerable time, and finally it was concluded that the discrepancy between rapid ("dynamic") and slow loading ("static") calibrations was of a small order of magnitude and was independent of the rate of loading over the range explored. At the computed point of balance of the pressures on the two sides of the orifice the deflexion of the diaphragm appeared to be about 3 parts in 1000 less than that given by a "static" calibration. This defect of 0·3 % disappeared in about 0·05 sec. In analysing the explosion records this correction has been applied without making any further attempt to confirm it. The corrections were determined at room temperature and applied to calibrations at 100° C.

In making a "static" calibration at 100° C, the explosion vessel itself was charged with air, or other convenient gas, to a known pressure or series of known pressures—the pressures being measured to within 0·02 lb. per sq. in. by means of a standard oil column and dead-weight loading device (Glazebrook 1922). The loading was usually followed by a similar unloading process, and at each pressure the position of the light spot was recorded on sensitized paper. The photographic record was measured by means of a travelling microscope in the same way as the explosion records. Static calibrations were numerous and probably averaged one to every four or five explosion records. They proved to be consistent enough to justify the taking of a mean spread over a period of a year or more.

The consistency of the recording of the explosion pressure can be judged from an examination of the closeness with which the calculated maximum explosion temperatures repeat for the same mixture. Taking from Tables II, III, IV, V, VII, VIII and IX all the explosions without the cage—except those in which water vapour additions were made to the charge—it will be found that these temperatures repeat *on the average* to within 1 part in 1000. This indicates that in general the explosion pressures were recorded consistently and that measurements of the explosion record could be made with considerable precision. There are some marked departures from this general order of "repeatability", particularly where the pressures are low and the explosion times short.

(*d*) *The initial pressure gauge.* For the experiments detailed in this report, the Bourdon gauge that had been previously used was replaced by a mercury U-tube some 3 m. in height in order that the desired "repeatability" of the explosion pressure might not be adversely affected by insufficient precision in the measurement of the initial pressures.

This U-tube is provided with a calibrated steel scale and special reading devices, and the whole is enclosed in a glass-windowed case within which air is caused to circulate and thus maintain an atmosphere of uniform temperature.

(*e*) *Mixing cylinders.* The gas mixtures were made up in bulk so as to provide sufficient for a series of explosions. Two types of mixing cylinder were used. One consisted of a standard steel cylinder as employed for the commercial distribution of compressed hydrogen: its capacity was about $23\frac{1}{2}$ l. and the mixing of its gaseous contents was effected by jacketing its upper end with ice and immersing its lower end in a bath of boiling water for an hour or more, the time depending on the relative density of the various gases in the mixture and the order in which they were introduced into the mixing cylinder. This type was unsuitable where rapid and frequent adjustments in mixture composition were required, and to meet these conditions a steel cylinder having a mechanical stirring device was employed. This cylinder—of some 28 l. capacity—was provided with trunnions on which it could be readily tilted so as to cause an internal stirrer to traverse its entire length. Mixing was effected by continuing the backward and forward tilting process for ten minutes or more.

(*f*) *Apparatus for determining the mixture composition.* All the mixtures used in this investigation were rich in the sense that they contained more combustible gas than could combine with the oxygen (or nitrous oxide) present. Since, therefore, the oxygen or nitrous oxide content gave a measure of the heat of reaction, it was necessary to determine its amount with a high degree of precision. A calorimetric method was therefore adopted in place of the direct volumetric determinations associated with the earlier experiments. The adiabatic bomb calorimeter, that had been specially designed for making a redetermination of the heat of formation of nitrous oxide, was used for the purpose. A sample of each mixture was exploded in the bomb and its oxygen, or nitrous oxide, content computed from the heat generated. Details of the bomb calorimeter and the experimental technique employed have already been published (Fenning and Cotton 1933).

In the case of other constituents of the mixture, volumetric determinations were made by means of a Macfarlane and Caldwell gas analysis apparatus and a somewhat specialized technique. The determination of the impurities in individual gases, on the other hand, might call for some special procedure or device. In the case of argon, for example, the analysis made by the Chemical Research Laboratory, Teddington, involved considerable elaboration.

(*g*) *Apparatus for determining the compressibility of gas mixtures.* Information as to the compressibility characteristics of the various gas mixtures was required, first, in connexion with the bomb calorimeter determination of their oxygen contents and, secondly, in regard to the initial pressure and temperature conditions of the charge in the explosion vessel. Apparatus was therefore devised for the purpose. It comprised a steel pressure vessel of known volume which could be charged to the required pressure and a system of calibrated glass vessels for measuring the gas discharged from the pressure vessel when its contents were expanded to atmospheric pressure. The apparatus and its method of use for obtaining compressibility data at both 20 and 100° C are described in detail in the Supplement, and hence all that need be given here is a brief account of the use of the apparatus in connexion with the bomb calorimeter. In making oxygen determinations by means of that calorimeter it became the standard practice to charge the bomb and the pressure vessel simultaneously so that pressures, temperatures and gas mixture compositions were the same in each. The charge in the pressure vessel was then expanded to atmospheric pressure and its volume determined at 20° C, whereas the charge in the bomb was exploded and from the heat generated its oxygen content at atmospheric pressure and 20° C was computed. Knowing the relative volumes of pressure vessel and bomb, the percentage oxygen content of the mixture at atmospheric pressure could be deduced. This method avoids the precise measurements of charging pressure and temperature of the bomb that would be required if the computations were based on independent determinations of the compressibility of the gas mixture.

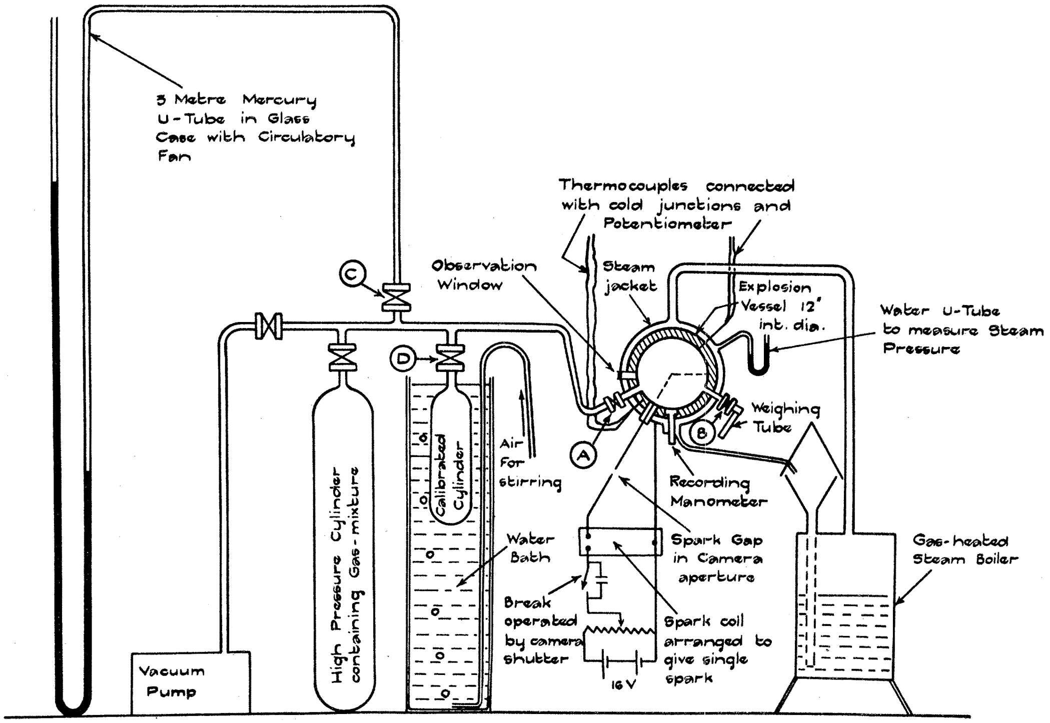

FIG. 8. Apparatus used in making mixtures of water vapour and gas mixtures.

(*h*) *Apparatus and technique for the addition of water vapour to certain gas mixtures.* In the experiments for the determination of the molecular heats of hydrogen and water vapour, considerable quantities of water vapour were added to some of the gas mixtures. In order to obtain the required proportions of water vapour and gas mixture, the former was weighed as a liquid and the latter measured on a volume and pressure basis, the necessary experiments being made to determine the departure of the gas mixture from perfect gas behaviour. Fig. 8 gives a diagrammatic representation of the apparatus and shows the calibrated cylinder for measuring the gas mixture and, to an exaggerated scale, the small phosphor-bronze tube in which the water was weighed. The volume of the calibrated cylinder, which was carefully determined, was about one-third that of the explosion vessel.

The mixture of water vapour and gas mixture was made up for each experiment in the explosion vessel itself, the latter being maintained at 100° C. The calibrated cylinder was charged with gas mixture to the requisite pressure and the temperature of its water-bath noted. The explosion vessel was evacuated, washed out with a small quantity of the gas mixture, and re-evacuated until the pressure was within 2 or 3 mm. of mercury. The weighing tube containing the required quantity of water was then coupled to the coned outlet of valve *B* and this valve opened after valve *A* had been closed. By applying a gas flame to the top of the weighing tube and working gradually downwards, the water it contained was evaporated and the steam formed passed through the electrically heated body of the valve *B* into the explosion vessel. The pressure of the water vapour was then measured on the U-tube, the pipe-line between the explosion vessel and the U-tube having been charged previously with gas mixture to the expected pressure. Valve *A* was then closed and the pressure in the pipe-line raised to the value it was expected would be reached when the charge of gas mixture in the calibrated cylinder was added to the water vapour. Valve *C* was then closed temporarily, and the opening of valve *A* was followed by as rapid an opening of the valve *D* as possible in order to rush the gas portion of the charge into the explosion vessel and so aid its mixture with the water vapour already there. After the lapse of a few minutes, the pressures were read on the U-tube and readings were taken of the pressure of the steam-bath surrounding the explosion vessel and of the temperature of the water-bath containing the calibrated cylinder. As the original charging pressure and temperature of the calibrated cylinder were known, the quantity of mixture discharged from it could be determined from the initial and final pressure and temperature readings—allowance being made for any failure to charge the connecting tubes to the correct pressures.

The charging pressure of the calibrated cylinder was outside the range of the mercury U-tube and was measured by means of a calibrated Bourdon pressure gauge, whereas the temperature of its water-bath, which was maintained at about 20° C, was determined by means of a Black's thermometer graduated to 0·01° C.

It may be mentioned that a convenient method of following the evaporation of the water in the weighing tube consisted of applying a wet camel-hair brush to the *outside* of the tube and noting the line of demarcation between slow and rapid evaporation of the applied water.

3. The experiments and their results

(*a*) *Foreword.* Several series of experiments, which were carried out in the earlier stages of the investigation, have had to be discarded owing largely to the difficulties experienced in eliminating, or allowing for, the loss of heat to the walls of the explosion vessel during the development of the explosion pressure.

Although some of the early series of experiments had features of particular interest, it seems advisable to restrict the present paper to the more adequate experiments that have superseded them. The latter experiments comprise four series in which an attempt was made to match the heat losses during the pressure-rise period and a variety of explosions in which the heat loss during that period was determined by means of the "cage" already described.

(*b*) *The explosion temperature.* The rise of pressure which takes place on the explosion of a gaseous mixture in a closed vessel or bomb is due to three factors, namely: (i) the rise in temperature of the explosion-vessel contents brought about by the conversion of chemical energy into heat energy, (ii) the variation in the number of molecules, i.e. molecular concentration, owing to chemical combinations and dissociations, and (iii) changes in compressibility characteristics of the gaseous contents of the bomb.

The conditions under which combustion takes place suggest that, at the moment of the *recorded* maximum pressure in a comparatively rapid explosion, there may be a temperature gradient of several hundred degrees in the high-temperature gaseous mass, and that the temperature distribution may be such as is shown in figs. 11 and 12. With this temperature gradient will be associated a corresponding variation in molecular concentration, and hence the recorded explosion pressure will be a measure of the summation of the products of the temperature and molecular concentrations of the elementary fractions composing the whole mass. If this product changes when the temperature of the gaseous mass is equalized (without loss in internal energy), then the pressure will also change, *but the value attained will be that from which the gas temperature required for specific heat determinations should be derived.*

The question of the change of pressure that takes place when the temperature of the gaseous mass is equalized has been examined by Lewis and von Elbe (1934*a*, *b*, *c*) in the case of certain mixtures involving the combustion of hydrogen or the decomposition of ozone. In the particular case of these hydrogen mixtures at their particular initial pressures, these investigators found that the equalization of temperature caused a rise of pressure of from about 0·2 to 0·8 %, the amount varying with the explosion temperature and the nature of the diluent, whereas in the ozone mixtures the change in pressure was still less.

These comparatively small effects did not encourage the computation of similar corrections in connexion with the present investigation until it was realized that the *variation* in the correction with the type of mixture, and particularly the higher order of the correction associated with the argon-diluted mixtures, might be significant. The subsequent expenditure of some months on the computation of gradient corrections was justified, for it rendered possible the satisfactory interpretation of experimental results which had hitherto proved intractable.

In view of the critical nature of these gradient corrections on certain experiments in the present research, it is desirable to refer to their determination in some detail.

During the passage of the flame from the central ignition point to the boundary walls of the vessel, each elementary fraction of the whole gaseous mass can be regarded as being burnt at constant pressure. The first fraction burns at the initial pressure of the charge and is subsequently compressed through the ratio of the maximum explosion pressure to the initial charge pressure, whereas the last fraction is first compressed in its unburnt state through that ratio and then burnt at the explosion pressure. Intermediate fractions are compressed both before and after combustion, the compression ratio before combustion increasing and that after combustion decreasing as the proportion of the total charge burnt increases.

By considering the processes to which elementary fractions—distributed throughout the whole mass—are subjected, the temperatures, molecular concentrations and internal energies of these elementary fractions at the maximum pressure reached in the explosion can be computed. Curves showing, first, the value of the product of temperature and molecular concentration and, secondly, internal energy, for each elementary fraction in relation to its position in the general mass can then be plotted as shown in fig. 9. Graphical integration of the first curve gives the summation of the products of temperature and molecular concentrations on which the actual explosion pressure depends, whereas a similar process applied to the second curve gives the internal energy content of the whole mass from which the pressure associated with a uniform distribution of temperature can be computed. A correction is thus obtained for converting the *conventional* explosion temperature, based on the explosion pressure, into the *uniform* temperature associated with the same internal energy content of the whole mass.

Having outlined the method of computing the gradient correction, it is pertinent to add some particulars of assumptions made in tracing the history of elementary fractions of the gaseous mass. In determining the changes through which each elementary fraction passes it was assumed (i) that its rise of pressure before combustion was the same fraction of the total rise as the mass immediately preceding its combustion was of the whole mass; (ii) that its compression in the unburnt state was adiabatic; (iii) that its combustion took place at constant pressure without loss of heat; and (iv) that its subsequent compression to the maximum explosion pressure was adiabatic. For calculating the changes of temperature, due to compression and combustion, use was made of (i) the spectroscopic molecular heats, given in Table I, together with a value of 1·9869 cal./mol. for the gas constant R; (ii) the heats of combustion given in the introduction (p. 151) suitably adjusted to the temperature and pressure conditions; and (iii) the equilibrium constants given in the introduction (p. 150), although strictly these equilibrium equations relate to a narrower temperature range than the gradient correction calculations cover.

The calculation, by successive approximations, of the temperature of each elementary fraction before and after combustion presents no difficulty although it requires patience. The computation, by the same method, of the final compression temperature, is greatly assisted by the construction, at the outset, of curves to show (*a*) the relation to temperature of the total internal energy (above 100° C) of the high-temperature gaseous mass at the maximum pressure reached in the explosion, and (*b*) the corresponding molecular concentration (see fig. 10). The final compression of each elementary

Table I. Values of mean specific heat at constant volume between 373·13° C abs. (100° C) and the temperature given—the values being calculated from certain published values of constant-pressure specific heats deduced from spectroscopic data

Temperature °C abs.	Temperature °C	CO Johnston and Davis	CO_2 Kassel	H_2 Davis and Johnston	H_2O (gas) Gordon	OH Johnston and Dawson	O_2 Johnston and Walker	ON Johnston and Chapman	N_2 Johnston and Davis	N_2O Kassel
373·13	100	5·006	7·670	4·972	6·119	5·097	5·158	5·162	4·991	8·025
475	202	5·053	8·107	4·990	6·221	5·077	5·270	5·210	5·026	8·464
575	302	5·114	8·487	4·998	6·338	5·069	5·388	5·282	5·072	8·838
675	402	5·188	8·819	5·007	6·464	5·071	5·505	5·366	5·132	9·169
775	502	5·269	9·114	5·019	6·597	5·083	5·615	5·455	5·201	9·465
875	602	5·352	9·375	5·037	6·734	5·103	5·715	5·542	5·275	9·731
975	702	5·433	9·610	5·059	6·876	5·131	5·806	5·626	5·350	9·969
1075	802	5·511	9·821	5·087	7·020	5·166	5·887	5·704	5·424	10·184
1175	902	5·585	10·011	5·120	7·165	5·206	5·961	5·777	5·496	10·378
1275	1002	5·654	10·183	5·156	7·309	5·250	6·028	5·844	5·564	10·555
1375	1102	5·719	10·339	5·195	7·452	5·296	6·090	5·906	5·628	10·717
1475	1202	5·779	10·482	5·237	7·591	5·343	6·146	5·962	5·688	10·865
1575	1302	5·835	10·612	5·280	7·727	5·391	6·198	6·014	5·745	—
1675	1402	5·888	10·731	5·325	7·858	5·439	6·246	6·062	5·798	—
1775	1502	5·936	10·842	5·369	7·985	5·487	6·292	6·107	5·847	—
1875	1602	5·981	10·943	5·414	8·107	5·534	6·336	6·148	5·894	—
1975	1702	6·023	11·037	5·459	8·224	5·580	6·377	6·186	5·937	—
2075	1802	6·062	11·124	5·504	8·336	5·625	6·417	6·222	5·978	—
2175	1902	6·099	11·205	5·547	8·444	5·668	6·455	6·255	6·016	—
2275	2002	6·133	11·281	5·590	8·548	5·711	6·493	6·286	6·052	—
2375	2102	6·165	11·352	5·633	8·647	5·752	6·529	6·316	6·086	—
2475	2202	6·196	11·419	5·674	8·741	5·791	6·565	6·343	6·118	—
2575	2302	6·224	11·483	5·714	8·832	5·830	6·599	6·369	6·148	—
2675	2402	6·251	11·542	5·754	8·919	5·867	6·632	6·393	6·176	—
2775	2502	6·277	11·599	5·792	9·002	5·903	6·665	6·417	6·203	—
2875	2602	6·301	11·653	5·829	9·081	5·938	6·697	6·439	6·229	—
2975	2702	6·324	11·703	5·865	9·157	5·972	6·727	6·460	6·254	—
3075	2802	6·346	11·752	5·901	9·230	6·005	6·758	6·480	6·277	—
3175	2902	6·366	—	5·935	—	6·037	6·788	6·499	6·299	—
3275	3002	6·386	—	5·969	—	6·069	6·817	6·517	6·320	—
3375	3102	6·405	—	6·001	—	6·099	6·845	6·534	6·340	—
3475	3202	6·423	—	6·033	—	6·128	6·873	6·551	6·359	—
3575	3302	6·441	—	6·063	—	6·157	6·900	6·567	6·378	—
3675	3402	6·457	—	6·093	—	6·184	6·926	6·583	6·395	—

All values are given in calories per gram-molecule.

fraction must bring it to some point on these curves, and hence the curves provide the requisite data in regard to internal energy and molecular concentration for any guessed final temperature. In selecting the final temperature, so that the work done during compression may be equal to the increase in internal energy, use was made of the *apparent* molecular heat of the gas during compression, the apparent molecular heat being the change in internal energy per degree change in temperature and per mol. of the mean of the molecular concentrations before and after compression (see Appendix I, p. 207). The device of employing apparent molecular heats, in the case of dissociating gases, in order to find the temperature reached after expansion or compression, was adopted by Tizard and Pye (1923–4), and shown by them to give reasonably accurate results in the particular case they examined.

To save further description, and yet leave no doubt as to the method employed for calculating the gradient correction, an example is given in § 2 of Appendix I. The example relates to a simplified version of the nitrogen-diluted mixture of the third series of "Matched Explosions", and the curves of figs. 9 and 10 apply to the same mixture. The final result, in regard to the distribution of internal energy and of the product of temperature and molecular concentration, is shown by the curves in fig. 9, whereas curve 3 of fig. 11 illustrates the distribution of temperature.

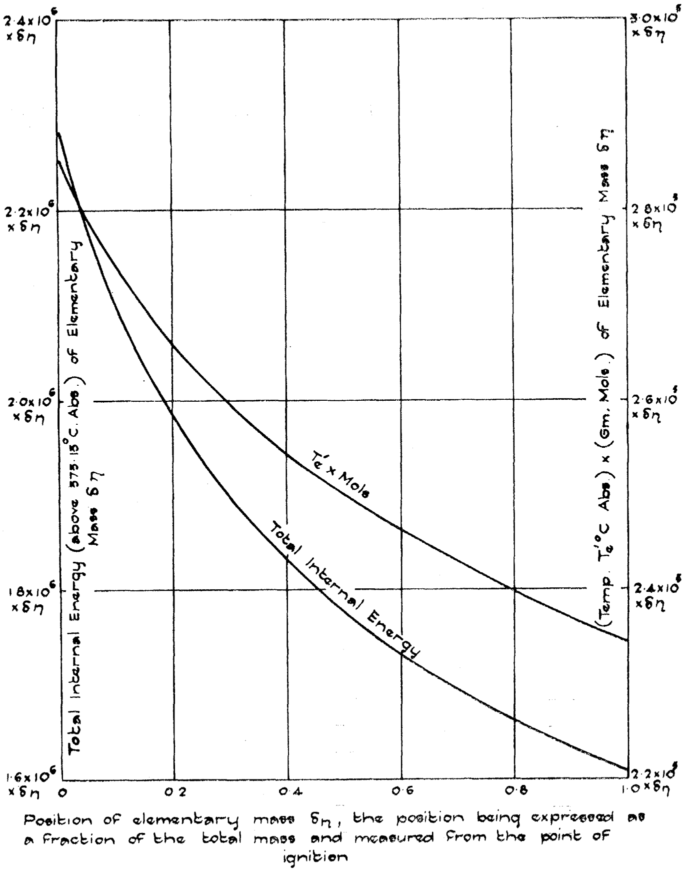

FIG. 9. Computed distribution of energy and $T_e' \times$ mol. at moment of attainment of maximum explosion pressure—basic mixture $48{\cdot}85\ CO + 13{\cdot}448\ O_2 + 37{\cdot}702\ N_2$ (similar to S 70*c*).

It has just been stated that the example taken relates to a simplified version of the actual experimental mixture, and from a comparison of the actual mixture as given in § 1 of Appendix I with the simplified mixture as given in § 2 of the same Appendix, it will be observed that the simplification consists in limiting the mixture to its main constituents. This process was deemed to be necessary in order to save time by reducing as far as possible the number of equations that have to be satisfied in order to comply with equilibrium conditions. Thus the exclusion of the small hydrogen content resulted

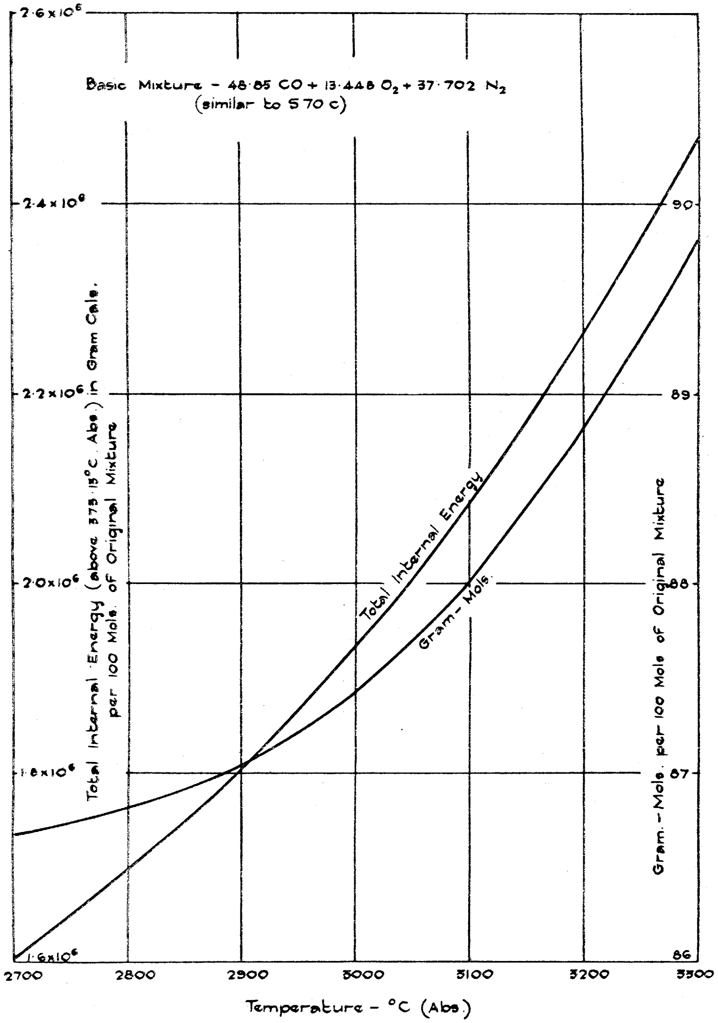

FIG. 10. Internal energy content and molecular concentration of a gas mixture in relation to temperature (at 25·07 atm.).

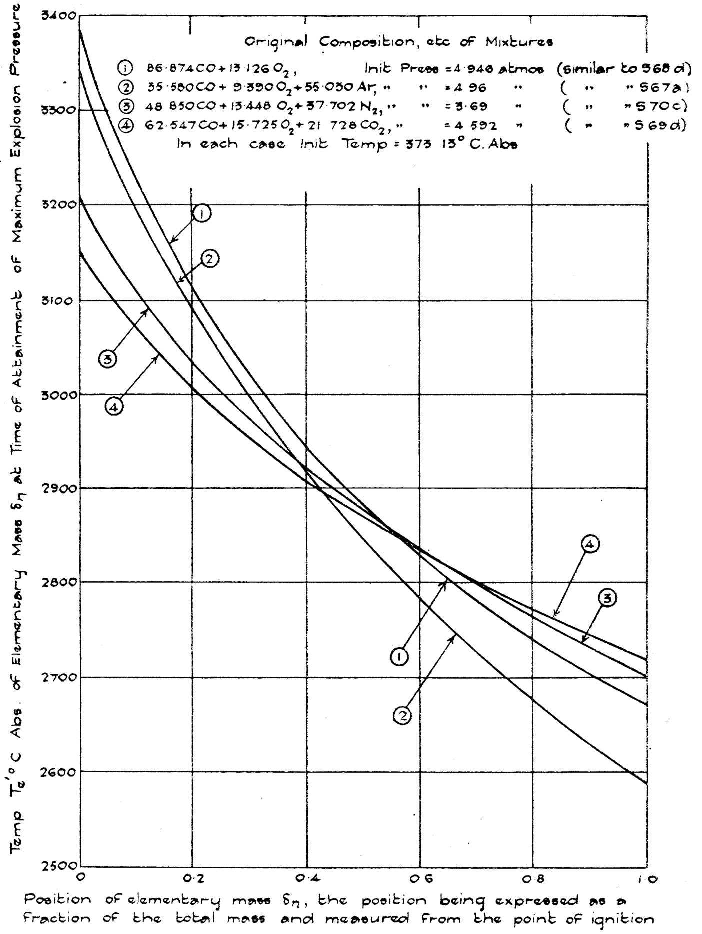

FIG. 11. Computed distribution of temperature at moment of attainment of maximum explosion pressure—Series 3 of "Matched Explosion" mixtures.

in a considerable saving in this respect without, it is hoped, greatly affecting the accuracy of the results.

It will be observed also that the oxygen content had to be reduced. This was required in order to compensate for the absence of heat loss and for the slightly lower molecular heats on which the computations were based. In the fourth series of the "Matched Explosions" this reduction in the oxygen content led to a considerable reduction in the degree of dissociation and hence, in selecting mixtures to represent the other three series, an attempt was made to counteract this feature by varying, where possible, the concentration of the gases which tended to suppress dissociation. This is referred to in § 2 of Appendix I.

The results of the temperature gradient calculations as a whole are given in Tables II–V, and although the corrections they indicate proved so effective in disposing of an apparent increase in the specific heat of argon it must be admitted that they are comparatively trifling in amount. Thus in the case of the argon-diluted mixture of the third series of "Matched Explosions" the equalization of the temperature gradient, shown by curve 2 of fig. 11, caused a pressure rise of about 1 %, whereas in the case of the carbon dioxide-diluted mixture of the same series (see curve 4 of fig. 11) the rise was only about one-third of this percentage. The much higher heat capacity of the latter mixture and its greater susceptibility to dissociation are illustrated by the considerable reduction in temperature gradient as compared with the argon-diluted mixture, as will be seen from a comparison of curves 4 and 2 of fig. 11.

Curves 1 and 3 of the same figure (fig. 11) illustrate the effect of replacing carbon monoxide by nitrogen and thereby increasing the dissociation, although a small portion of the increase must be attributed to a reduction in the explosion pressure arising from the lower initial pressure.

The curves of fig. 12 represent the temperature gradient in four argon-diluted mixtures having the same initial pressure but varying explosion temperatures. Here again the flattening effect of dissociation is seen as the temperature is raised and dissociation becomes more pronounced.

Gradient corrections have been computed for the majority of the experiments on which the molecular heats of carbon dioxide, carbon monoxide and nitrogen are based, and also for two pairs of mixtures relating to hydrogen and water vapour.

(*c*) *The " Matched Explosion" series of experiments for the determination of the molecular heats of* CO, N_2 *and* CO_2. These explosion experiments were designed to enable the molecular heats of carbon monoxide, carbon dioxide and nitrogen to be determined without recourse to the very difficult measurement of the quantity of heat absorbed by the walls of the explosion vessel during the comparatively short interval between the passage of the igniting spark and the attainment of the maximum explosion pressure.

The objectives were, first, the use of argon as a standard of heat capacity and, secondly, the adjustment of the loss of heat to the walls of the vessel so as to make it a constant proportion of the heat arising from the chemical reaction.

If, in the explosion of a gas mixture of the type

$$(2+n)\,CO+O_2+b\,.\,Ar,$$

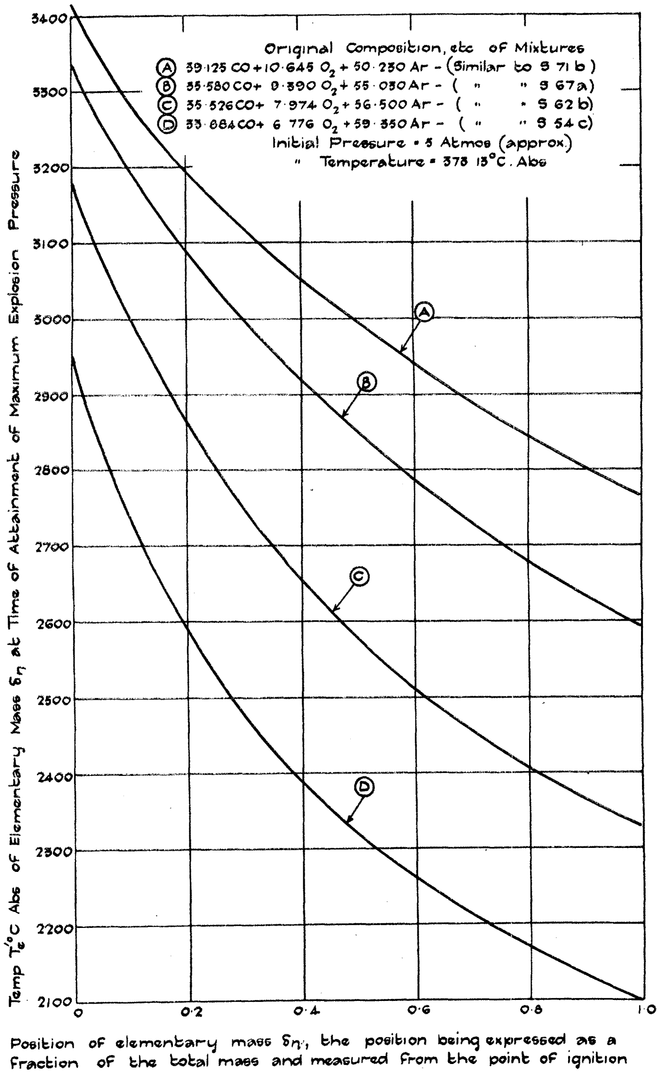

FIG. 12. Computed distribution of temperature at moment of attainment of maximum explosion pressure—argon mixtures.

the argon can be replaced by $d\,.\,CO$ or $e\,.\,N_2$ or $f\,.\,CO_2$ without affecting either the rise of temperature (T_m-T_i) on explosion, or the chemical reactions during the pressure-rise period, or the percentage of the heat of reaction absorbed by the walls of the explosion vessel during the same period, then

$$C_{CO}=\frac{b}{d}C_{Ar};\quad C_{N_2}=\frac{b}{e}C_{Ar};\quad C_{CO_2}=\frac{b}{f}C_{Ar},$$

where C_{CO}, C_{N_2}, etc. represent the mean molecular heats at constant volume of carbon monoxide, nitrogen, etc. over the temperature range T_i to T_m. Since the molecular heat of argon is considered to be constant—except at temperatures much in excess of

TABLE II. EXPERIMENTAL AND OTHER DATA RELATING TO SERIES 1 OF THE "MATCHED EXPLOSIONS"

Mixture no. and "*PV*" ratio	"Cage"	Initial conditions		Explosion time sec.	Max. press. from explosion record P_e atm.	Temp. corresponding to P_e T_e °C abs.	Temp. 0·1 sec. after T_e, $T_{1/10}$ °C abs.	Temp. gradient correction °C		Mixture composition in gram-molecules										
		Temp. T_i °C abs.	Press. P_i atm.							CO_2	CO	H_2O (gas)	H_2	H	OH	O_2	O	NO	N_2	Ar
S 54*c* and 1·0009	No	373·4	5·003	0·108	29·55	2374	2236	3	Initially	0·020	33·492	—	0·720	—	—	7·045	—	—	0·410	58·313
	,,	373·7	5·057	0·105	29·82	2372	2232	3	At T=2373°	13·535	19·977	0·558	0·149	0·010	0·014	0·001	—	0·001	0·410	58·313
	,,	373·6	5·010	0·106	29·55	2373	2228	3	At T=2232°	13·548	19·964	0·556	0·158	0·005	0·006	—	—	—	0·410	58·313
									At T=2376°	13·535	19·977	0·559	0·149	0·010	0·014	0·001	—	0·001	0·410	58·313
									Gradient mixture:											
									Initially	—	33·884	—	—	—	—	6·766	—	—	—	59·350
									At T=2373°	13·531	20·353	—	—	—	—	0·001	—	—	—	59·350
S 55*n* and 1·0013	No	373·5	3·686	0·106	21·03	2373	2234	−0·1	Initially	—	89·415	—	0·210	—	—	10·075	—	—	0·300	—
	,,	373·4	3·686	0·107	21·03	2372	2238	−0·1	At T=2373°	20·019	69·396	0·125	0·078	0·009	0·005	—	—	—	0·300	—
									At T=2236°	20·024	69·391	0·124	0·083	0·004	0·002	—	—	—	0·300	—
									Gradient mixture:											
									Initially	—	90·243	—	—	—	—	9·757	—	—	—	—
									At T=2373°	19·514	70·729	—	—	—	—	—	—	—	—	—
S 56*d* and 1·0016	No	373·0	3·608	0·104	20·66	2378	2237	2	Initially	0·050	47·509	—	0·400	—	—	10·034	—	—	41·587	0·420
	,,	373·1	3·607	0·104	20·62	2373	2237	2	At T=2376°	19·784	27·775	0·310	0·079	0·009	0·013	0·001	0·001	0·009	41·582	0·420
	,,	373·1	3·610	0·103	20·66	2377	2240	2	At T=2238°	19·798	27·761	0·311	0·084	0·005	0·005	—	—	0·003	41·586	0·420
									At T=2378°	19·784	27·775	0·311	0·079	0·009	0·013	0·001	0·001	0·009	41·582	0·420
									Gradient mixture:											
									Initially	—	46·746	—	—	—	—	9·729	—	—	43·525	—
									At T=2376°	19·447	27·299	—	—	—	—	0·001	0·001	0·009	43·520	—
S 57*c* and 0·9994	No	373·7	3·092	0·106	17·04	2363	2225	1·5	Initially	33·640	52·195	—	0·900	—	—	12·885	—	—	0·380	—
	,,	373·9	3·092	0·106	17·05	2365	2225	1·5	At T=2364°	58·546	27·289	0·809	0·068	0·008	0·036	0·007	0·001	0·003	0·379	—
	,,	373·7	3·208	0·106	17·69	2363	2228	1·5	At T=2226°	58·574	27·261	0·817	0·074	0·004	0·015	0·001	—	0·001	0·380	—
									At T=2365°	58·546	27·289	0·809	0·068	0·008	0·036	0·007	0·002	0·003	0·379	—
									Gradient mixture:											
									Initially	34·473	53·000	—	—	—	—	12·527	—	—	—	—
									At T=2364°	59·511	27·962	—	—	—	—	0·007	0·001	—	—	—
S 58*e* and 1·0004	No	373·8	3·288	0·106	18·37	2366	2227	1	Initially	20·236	67·384	—	0·420	—	—	11·700	—	—	0·260	—
	,,	373·7	3·289	0·105	18·37	2365	2225	1	At T=2366°	43·272	44·348	0·344	0·064	0·008	0·016	0·001	0·001	0·001	0·259	—
									At T=2226°	43·283	44·337	0·346	0·069	0·004	0·006	—	—	—	0·260	—
									At T=2367°	43·272	44·348	0·344	0·064	0·008	0·016	0·001	0·001	0·001	0·259	—
									Gradient mixture:											
									Initially	20·900	67·680	—	—	—	—	11·420	—	—	—	—
									At T=2366°	43·736	44·844	—	—	—	—	0·002	0·001	—	—	—
S 59*b* and 1·0008	No	373·6	4·007	0·176	23·72	2382	2254	Not calc.	Initially	0·015	33·561	—	0·210	—	—	7·092	—	—	0·410	58·712
	,,	373·8	4·011	0·176	23·67	2376	2248		At T=2378°	14·026	19·551	0·162	0·041	0·006	0·009	0·001	—	0·001	0·410	58·712
	,,	373·4	4·013	0·176	23·71	2376	2248		At T=2250°	14·031	19·545	0·163	0·044	0·003	0·004	—	—	—	0·410	58·712
	Yes	373·8	4·011	0·175	23·32	2341	—		At T=2342°	14·028	19·548	0·162	0·042	0·005	0·007	0·001	—	0·001	0·410	58·712
	,,	373·9	4·018	0·175	23·38	2343	—													
S 60*f* and 1·0014	No	373·3	2·859	0·177	16·40	2390	2260	Not calc.	Initially	0·020	47·329	—	0·120	—	—	10·311	—	—	41·760	0·460
	,,	373·2	2·861	0·176	16·42	2392	2259		At T=2391°	20·526	26·823	0·091	0·021	0·006	0·009	0·001	0·001	0·012	41·754	0·460
	Yes	373·7	2·857	0·176	16·12	2354	—		At T=2260°	20·540	26·809	0·093	0·023	0·003	0·004	—	—	0·004	41·758	0·460
	,,	373·8	2·864	0·175	16·19	2359	—		At T=2356°	20·531	26·818	0·092	0·022	0·005	0·007	0·001	0·001	0·009	41·755	0·460
	,,	373·7	2·867	0·176	16·19	2356	—													

TABLE III. EXPERIMENTAL AND OTHER DATA RELATING TO SERIES 2 OF THE "MATCHED EXPLOSIONS"

		Initial conditions								Mixture composition in gram-molecules											
Mixture no. and "PV" ratio	"Cage"	Temp. T_i °C abs.	Press. P_i atm.	Explosion time sec.	Max. press. from explosion record P_e atm.	Temp. corresponding to P_e T_e °C abs.	Temp. 0·1 sec. after T_e, $T_{1/10}$ °C abs.	Temp. gradient correction °C		CO_2	CO	H_2O (gas)	H_2	H	OH	O_2	O	NO	N_2	N	Ar
S 62*b*	No	374·1	4·993	0·079	32·19	2633	2457	13·5	Initially	0·050	35·891	—	0·630	—	—	8·413	—	—	0·390	—	54·626
and	,,	374·0	5·001	0·079	32·29	2637	2459	13·5	At $T=2635°$	16·294	19·647	0·492	0·097	0·024	0·058	0·011	0·005	0·005	0·388	—	54·626
1·0008	,,	373·3	4·998	0·079	32·30	2634	2456	13·5	At $T=2457°$	16·340	19·601	0·506	0·106	0·012	0·024	0·002	0·001	0·002	0·389	—	54·626
									At $T=2648°$	16·288	19·653	0·491	0·096	0·025	0·062	0·012	0·006	0·005	0·387	—	54·626
									Gradient mixture:												
									Initially	—	35·526	—	—	—	—	7·974	—	—	—	—	56·500
									At $T=2635°$	15·923	19·604	—	—	—	—	0·010	0·005	—	—	—	56·500
S 63*a*	No	374·3	4·727	0·082	29·40	2637	2470	2	Initially	0·060	87·763	—	0·200	—	—	11·617	—	—	0·360	—	—
and	,,	374·2	4·725	0·083	29·39	2637	2464	2	At $T=2637°$	23·141	64·682	0·124	0·056	0·019	0·020	0·002	0·002	0·002	0·359	—	—
1·0016	,,	373·7	4·722	0·082	29·41	2636	2466	2	At $T=2467°$	23·155	64·668	0·128	0·062	0·010	0·009	—	—	0·001	0·360	—	—
	Yes	373·9	4·726	0·082	29·19	2616	—	—	At $T=2639°$	23·141	64·682	0·124	0·056	0·019	0·020	0·002	0·002	0·002	0·359	—	—
	,,	373·8	4·730	0·082	29·23	2617	—	—	At $T=2617°$	23·144	64·679	0·125	0·057	0·018	0·018	0·002	0·002	0·002	0·359	—	—
									Gradient mixture:												
									Initially	—	88·692	—	—	—	—	11·308	—	—	—	—	—
									At $T=2637°$	22·610	66·082	—	—	—	—	0·002	0·002	—	—	—	—
S 64*d*	No	373·2	4·154	0·079	25·18	2630	2464	5·5	Initially	24·247	60·661	—	0·610	—	—	14·132	—	—	0·350	—	—
and	,,	373·2	4·154	0·079	25·18	2630	2465	5·5	At $T=2630°$	51·813	33·095	0·505	0·053	0·019	0·087	0·044	0·011	0·009	0·345	—	—
0·9994	Yes	373·4	4·155	0·079	24·99	2611	—	—	At $T=2465°$	51·922	32·986	0·527	0·058	0·010	0·038	0·009	0·002	0·003	0·348	—	—
	,,	373·4	4·154	0·079	24·99	2611	—	—	At $T=2635°$	51·806	33·102	0·503	0·052	0·020	0·089	0·046	0·011	0·009	0·345	—	—
									At $T=2611°$	51·832	33·076	0·508	0·053	0·018	0·080	0·037	0·009	0·008	0·346	—	—
									Gradient mixture:												
									Initially	25·284	60·993	—	—	—	—	13·723	—	—	—	—	—
									At $T=2630°$	52·632	33·645	—	—	—	—	0·044	0·011	—	—	—	—
S 65*c*	No	373·3	4·632	0·078	28·89	2638	2472	7	Initially	0·040	51·597	—	0·380	—	—	11·653	—	—	35·890	—	0·440
and	,,	373·3	4·632	0·077	28·90	2639	2468	7	At $T=2638°$	22·937	28·700	0·288	0·059	0·020	0·046	0·011	0·005	0·048	35·865	0·002	0·440
1·0015	Yes	373·0	4·626	0·078	28·69	2620	—	—	At $T=2470°$	23·005	28·633	0·300	0·065	0·011	0·020	0·002	0·001	0·016	35·882	0·001	0·440
	,,	372·9	4·642	0·077	28·77	2618	—	—	At $T=2645°$	22·932	28·705	0·288	0·058	0·020	0·048	0·012	0·006	0·050	35·864	0·003	0·440
									At $T=2619°$	22·948	28·689	0·290	0·059	0·019	0·042	0·009	0·005	0·042	35·868	0·002	0·440
									Gradient mixture:												
									Initially	—	50·806	—	—	—	—	11·310	—	—	37·884	—	—
									At $T=2638°$	22·544	28·262	—	—	—	—	0·011	0·005	0·049	37·858	0·002	—

TABLE IV. EXPERIMENTAL AND OTHER DATA RELATING TO SERIES 3 OF THE "MATCHED EXPLOSIONS"

Mixture no. and "PV" ratio	"Cage"	Initial conditions		Explosion time sec.	Max. press. from explosion record P_e atm.	Temp. corresponding to P_e T_e °C abs.	Temp. 0·1 sec. after T_e, $T_{1/10}$ °C abs.	Temp. gradient correction °C		Mixture composition in gram-molecules											
		Temp. T_i °C abs.	Press. P_i atm.							CO_2	CO	H_2O (gas)	H_2	H	OH	O_2	O	NO	N_2	N	Ar
S 67*a* and 1·0009	No	373·4	4·993	0·059	35·00	2905	2709	28	Initially	0·090	36·611	—	0·660	—	—	10·189	—	—	0·380	—	52·070
	,,	373·7	4·997	0·059	35·01	2905	2706	28	At T=2905°	19·346	17·355	0·468	0·062	0·049	0·211	0·179	0·057	0·028	0·365	0·001	52·070
									At T=2708°	19·740	16·961	0·525	0·072	0·027	0·100	0·040	0·013	0·010	0·375	—	52·070
									At T=2933°	19·247	17·454	0·457	0·061	0·053	0·231	0·216	0·069	0·032	0·363	0·001	52·070
									Gradient mixture:												
									Initially	—	35·580	—	—	—	—	9·390	—	—	—	—	55·030
									At T=2905°	18·395	17·185	—	—	—	—	0·165	0·055	—	—	—	55·030
S 68*d* and 1·0014	No	373·6	4·977	0·059	33·70	2927	2714	9	Initially	0·030	85·900	—	0·190	—	—	13·592	—	—	0·288	—	—
	,,	373·7	4·990	0·059	33·81	2930	2717	9	At T=2929°	26·930	59·000	0·103	0·033	0·038	0·069	0·036	0·028	0·012	0·282	0·001	—
	Yes	372·8	4·975	0·058	33·54	2909	—	—	At T=2716°	27·038	58·892	0·122	0·042	0·021	0·031	0·007	0·006	0·004	0·286	—	—
	,,	372·8	4·978	0·059	33·57	2910	—	—	At T=2938°	26·922	59·008	0·102	0·033	0·039	0·071	0·038	0·030	0·012	0·281	0·001	—
									At T=2909°	26·947	58·983	0·105	0·034	0·037	0·065	0·031	0·024	0·010	0·282	0·001	—
									Gradient mixture:												
									Initially	—	86·874	—	—	—	—	13·126	—	—	—	—	—
									At T=2929°	26·162	60·712	—	—	—	—	0·032	0·026	—	—	—	—
S 69*d* and 0·9998	No	373·7	4·618	0·060	30·22	2897	2723	9	Initially	20·445	62·380	—	0·530	—	—	16·235	—	—	0·410	—	—
	,,	373·7	4·618	0·059	30·22	2897	2721	9	At T=2897°	51·408	31·417	0·365	0·033	0·036	0·227	0·393	0·086	0·043	0·388	0·001	—
	Yes	373·6	4·603	0·059	29·95	2881	—	—	At T=2722°	52·126	30·699	0·420	0·039	0·022	0·120	0·104	0·023	0·018	0·401	—	—
	,,	373·4	4·626	0·059	30·12	2882	—	—	At T=2906°	51·348	31·477	0·362	0·033	0·037	0·234	0·418	0·091	0·045	0·387	0·001	—
									At T=2882°	51·505	31·320	0·371	0·034	0·035	0·216	0·353	0·077	0·040	0·390	0·001	—
									Gradient mixture:												
									Initially	21·728	62·547	—	—	—	—	15·725	—	—	—	—	—
									At T=2897°	52·303	31·972	—	—	—	—	0·395	0·086	—	—	—	—
S 70*c* and 1·0016	No	373·0	3·721	0·059	25·07	2906	2698	11	Initially	0·051	49·852	—	0·431	—	—	14·008	—	—	35·231	—	0·427
	,,	373·5	3·722	0·059	25·06	2908	2704	11	At T=2907°	26·666	23·237	0·278	0·036	0·043	0·192	0·259	0·080	0·334	35·059	0·012	0·427
	Yes	373·4	3·719	0·059	24·87	2889	—	—	At T=2701°	27·401	22·503	0·330	0·043	0·024	0·091	0·056	0·017	0·116	35·171	0·004	0·427
	,,	373·4	3·720	0·059	24·89	2891	—	—	At T=2918°	26·600	23·303	0·274	0·036	0·044	0·199	0·279	0·087	0·351	35·049	0·012	0·427
									At T=2890°	26·759	23·144	0·283	0·037	0·041	0·182	0·232	0·072	0·309	35·071	0·010	0·427
									Gradient mixture:												
									Initially	—	48·850	—	—	—	—	13·448	—	—	37·702	—	—
									At T=2907°	25·970	22·880	—	—	—	—	0·253	0·079	0·341	37·526	0·012	—

TABLE V. EXPERIMENTAL AND OTHER DATA RELATING TO SERIES 4 OF THE "MATCHED EXPLOSIONS"

Mixture no. and "*PV*" ratio	"Cage"	Initial conditions		Explosion time sec.	Max. press. from explosion record P_e atm.	Temp. corresponding to P_e T_e °C abs.	Temp. 0·1 sec. after T_e, $T_{1/10}$ °C abs.	Temp. gradient correction °C		Mixture composition in gram-molecules											
		Temp. T_i °C abs.	Press. P_i atm.							CO_2	CO	H_2O (gas)	H_2	H	OH	O_2	O	NO	N_2	N	Ar
S 71*b* and 1·0007	No	373·6	4·995	0·049	36·29	3037	2842	20	Initially	0·070	37·032	—	0·705	—	—	11·581	—	—	0·380	—	50·232
	,,	373·3	4·994	0·048	36·32	3037	2842	20	At $T=3037°$	20·957	16·145	0·444	0·049	0·064	0·361	0·622	0·165	0·061	0·349	0·002	50·232
									At $T=2842°$	22·043	15·059	0·531	0·055	0·038	0·200	0·192	0·047	0·027	0·366	0·001	50·232
									At $T=3056°$	20·802	16·300	0·434	0·048	0·067	0·379	0·684	0·184	0·065	0·347	0·002	50·232
									Gradient mixture:												
									Initially	—	39·125	—	—	—	—	10·645	—	—	—	—	50·230
									At $T=3037°$	20·296	18·830	—	—	—	—	0·429	0·137	—	—	—	50·230
S 72*f* and 0·9997	No	373·7	4·254	0·048	28·72	3036	2890	2	Initially	22·211	56·363	—	0·690	—	—	20·306	—	—	0·430	—	—
	,,	373·7	4·254	0·049	28·71	3035	2892	2	At $T=3035°$	56·090	22·485	0·391	0·022	0·047	0·507	2·670	0·368	0·128	0·365	0·002	—
	Yes	373·4	4·251	0·048	28·59	3027	—	—	At $T=2891°$	58·987	19·587	0·473	0·023	0·031	0·357	1·381	0·164	0·080	0·390	0·001	—
	,,	373·5	4·250	0·048	28·55	3024	—	—	At $T=3037°$	56·054	22·520	0·390	0·022	0·047	0·508	2·685	0·371	0·129	0·365	0·002	—
									At $T=3025°$	56·332	22·242	0·397	0·023	0·045	0·496	2·562	0·349	0·124	0·367	0·002	—
									Gradient mixture:												
									Initially	22·210	59·272	—	—	—	—	18·518	—	—	—	—	—
									At $T=3035°$	55·171	26·311	—	—	—	—	1·883	0·309	—	—	—	—
S 73*c* and 1·0014	No	373·8	4·478	0·050	31·15	3039	2870	6	Initially	0·050	47·453	—	0·480	—	—	16·118	—	—	35·469	—	0·430
	,,	373·7	4·477	0·050	31·16	3040	2872	6	At $T=3039°$	28·737	18·766	0·268	0·025	0·049	0·325	0·984	0·221	0·766	35·076	0·020	0·430
	Yes	373·5	4·475	0·049	30·99	3026	—	—	At $T=2871°$	30·468	17·035	0·332	0·028	0·031	0·208	0·400	0·080	0·397	35·266	0·009	0·430
	,,	373·5	4·476	0·049	31·02	3028	—	—	At $T=3045°$	28·659	18·844	0·266	0·025	0·049	0·330	1·011	0·228	0·782	35·068	0·020	0·430
									At $T=3027°$	28·898	18·605	0·273	0·025	0·047	0·316	0·929	0·206	0·734	35·093	0·019	0·430
									Gradient mixture:												
									Initially	—	48·576	—	—	—	—	15·115	—	—	36·309	—	—
									At $T=3039°$	27·846	20·730	—	—	—	—	0·755	0·193	0·679	35·959	0·020	—
S 74*c* and 1·0016	No	373·7	3·068	0·048	21·45	3054	2766	13·5	Initially	0·030	84·799	—	0·210	—	—	14·721	—	—	0·240	—	—
	,,	373·6	3·070	0·047	21·44	3050	2765	13·5	At $T=3052°$	28·755	56·074	0·088	0·024	0·060	0·136	0·175	0·117	0·026	0·226	0·002	—
	Yes	373·6	3·068	0·048	21·27	3029	—	—	At $T=2765°$	29·223	55·606	0·129	0·038	0·031	0·055	0·022	0·015	0·007	0·237	0·001	—
	,,	373·6	3·069	0·048	21·27	3028	—	—	At $T=3065°$	28·711	56·118	0·086	0·024	0·061	0·140	0·190	0·127	0·028	0·225	0·002	—
									At $T=3029°$	28·826	56·003	0·092	0·026	0·057	0·128	0·151	0·101	0·024	0·227	0·002	—
									Gradient mixture:												
									Initially	—	85·888	—	—	—	—	14·112	—	—	—	—	—
									At $T=3055°$	27·799	58·089	—	—	—	—	0·157	0·112	—	—	—	—
S 71*a* and 1·0007	No	373·8	4·994	0·071	36·32	3043	2867	20	Initially	0·070	37·212	—	0·250	—	—	11·633	—	—	0·380	—	50·455
	,,	373·8	4·991	0·073	36·31	3044	2870	20	At $T=3043°$	21·377	15·905	0·122	0·013	0·033	0·197	0·698	0·179	0·065	0·347	0·002	50·455
									At $T=2869°$	22·457	14·826	0·161	0·016	0·022	0·125	0·251	0·060	0·032	0·364	0·001	50·455
									At $T=3062°$	21·216	16·066	0·117	0·013	0·035	0·205	0·765	0·198	0·069	0·345	0·002	50·455
									For details of mixture used in gradient calculations see S 71*b*												
S 72*c* and 0·9995	No	373·6	4·247	0·072	28·61	3033	2899	2	Initially	22·300	56·598	—	0·260	—	—	20·412	—	—	0·430	—	—
	,,	373·7	4·250	0·074	28·63	3033	2904	2	At $T=3033°$	56·722	22·176	0·108	0·006	0·024	0·268	2·762	0·372	0·130	0·364	0·002	—
	Yes	373·5	4·257	0·072	28·50	3020	—	—	At $T=2901°$	59·444	19·454	0·142	0·007	0·017	0·205	1·535	0·179	0·085	0·387	0·001	—
	,,	373·5	4·244	0·073	28·40	3019	—	—	At $T=3035°$	56·669	22·229	0·108	0·006	0·024	0·269	2·786	0·376	0·131	0·364	0·002	—
									At $T=3020°$	57·041	21·857	0·112	0·006	0·023	0·262	2·619	0·347	0·125	0·367	0·002	—
									For details of mixture used in gradient calculations see S 72*f*												

In this set the correction for equalization of temperature gradient was applied as an alteration in the maximum pressure and the corrected temperature was calculated to correspond.

those reached in the present experiments—the substitution of its value, 2·98, permits these molecular heats to be expressed in heat units.

If the conditions postulated could be realized in practice, a very simple method would be available for molecular heat determinations of suitable gases, and all that would be necessary would be to make the argon constituent as large a proportion of the whole mixture as is possible in order to reduce the multiplication of experimental errors. This latter precaution is of importance because, in the analysis of the results, the errors which relate to the heat capacity of the mixture as a whole are automatically assigned to the argon—or its equivalent—constituent, and the larger the latter the less their multiplication becomes.

As to the realization of the postulated conditions in practice, there should be no difficulty in adjusting the quantity of the gas that is substituted for the argon so as to maintain a constant rise of temperature on explosion—or in correcting for any small departure from constancy. The present investigation has, however, emphasized that it may be misleading to base the rise in temperature on the rise in pressure, without regard to a probable temperature gradient in the gaseous contents of the bomb.

The condition regarding the constancy of the chemical reactions cannot be fulfilled owing to the influence on those reactions of the gas that is substituted for argon. Thus carbon monoxide tends to suppress dissociation and carbon dioxide to augment it, whereas the presence of nitrogen leads to the formation of nitric oxide and a reduction in the formation of carbon dioxide. Fortunately, a considerable amount of data is now available from which the extent and nature of the chemical reactions can be computed, thus permitting an evaluation of the composition of the burnt gases under the explosion temperature and pressure conditions and also the quantity of heat arising from such reactions. Owing to this variation in the chemical reactions it is no longer possible to cancel from the burnt gas equations all gases except argon and its substitute. The quantities of the residual gases are often small, however, and their expression in terms of argon or its substitute provides a solution involving no serious error.

Having shown that the practical difficulties in regard to the first two conditions can be overcome, the success of the method seems to depend on the possibility of so controlling the absorption of heat by the vessel walls as to make it a constant proportion of the heat of reaction, and the fulfilment of this condition was sought by "matching" the explosions of a series so that approximately the same values were obtained for (i) the conventional explosion temperature, (ii) the explosion time, and (iii) the percentage heat loss during a short period (0·1 sec.) following the attainment of the maximum explosion pressure, the percentage being based on the heat of reaction or, if more convenient, on the heat imparted to the gases during the pressure rise period. The implication that the heat loss characteristics of a gas mixture during the spread of combustion can be inferred from measurements made when the combustion is more or less complete requires some discussion, but this will be deferred until the section on heat loss is reached (see p. 198).

As to the "matching" process, the explosion temperatures were balanced by varying the oxygen content of the mixture; the explosion times were equalized by varying the concentrations of the small quantity of hydrogen that must be added to give the mixture a reasonably short explosion time; and the rates of cooling were adjusted by varying the initial pressure of the mixture before explosion. The extreme sensitiveness of the explosion times of comparatively dry carbon monoxide-oxygen mixtures to small additions of hydrogen has already been demonstrated by Bone and Haward (1921) and Fenning (1926), and it is probably well known that the rate of cooling of a given explosive mixture is increased by reducing its density. The cooling in 0·1 sec. was computed from temperatures, etc. based on the pressures at the beginning and end of this interval, account being taken of the heat arising from any further combustion rendered possible by the change in the temperature and pressure conditions. No attempt was made to allow for any temperature gradient effects in calculating this loss of heat to the walls of the vessel or in relating this loss to the heat imparted to the gases during the pressure rise.

If the matching fulfils its function of equalizing the percentage heat losses prior to the attainment of the maximum explosion pressure, the mean heat capacities of the various gas mixtures between T_i and T_m are given by:

$$\text{(i)}\quad (2-w)\,C_{\mathrm{CO_2}}+(n+w)\,C_{\mathrm{CO}}+\frac{w-w'}{2}\,C_{\mathrm{O_2}}+w'.C_{\mathrm{O}}+b.C_{\mathrm{Ar}}=\{Q(2-w)-w'.Q'\}P,$$

$$\text{(ii)}\quad (2-x)\,C_{\mathrm{CO_2}}+(n+x)\,C_{\mathrm{CO}}+\frac{x-x'}{2}\,C_{\mathrm{O_2}}+x'.C_{\mathrm{O}}+d.C_{\mathrm{CO}}=\{Q(2-x)-x'.Q'\}P,$$

$$\text{(iii)}\quad (2-y)\,C_{\mathrm{CO_2}}+(n+y)\,C_{\mathrm{CO}}+\frac{y-y'}{2}\,C_{\mathrm{O_2}}+y'.C_{\mathrm{O}}+f.C_{\mathrm{CO_2}}=\{Q(2-y)-y'.Q'\}P,$$

$$\text{(iv)}\quad (2-z)\,C_{\mathrm{CO_2}}+(n+z)\,C_{\mathrm{CO}}+\frac{z-z'-z''}{2}\,C_{\mathrm{O_2}}+z'.C_{\mathrm{O}}+z''.C_{\mathrm{NO}}+i.C_{\mathrm{N}}+\left(e-\frac{z''+i}{2}\right)C_{\mathrm{N_2}}$$
$$=\{Q(2-z)-z'.Q'-z''.Q''-i.Q'''\}P,$$

where $2Q$, $2Q'$, $2Q''$ and $2Q'''$ represent the heats of formation, at constant volume and 100° C, of $2CO_2$ from $2CO+O_2$, O_2 from $O+O$, N_2+O_2 from $2NO$, and N_2 from $N+N$ respectively; and $(1-P)$ is the fraction of the heat of reaction which fails to reach the gas due to absorption by the vessel walls, etc. By expressing $C_{\mathrm{O_2}}$ and C_{NO} in terms of $C_{\mathrm{CO_2}}$, C_{CO} or $C_{\mathrm{N_2}}$ by the use of ratios obtained from, say, Table I, the unknown quantities can be reduced to four, viz. $C_{\mathrm{CO_2}}$, C_{CO}, $C_{\mathrm{N_2}}$ and P, and their values determined. Alternatively the molecular heats of CO, CO_2 and N_2 can be found in terms of the molecular heat of argon, as already indicated (see § 3 of Appendix I).

The quantity $(1-P)$ represents not only the loss of heat to the walls of the vessel, but also the loss due to any failure to burn the whole of the charge when the maximum pressure is reached. In the experiments of series 1 of the "Matched Explosions"—and to a less extent in series 2—the explosion records indicated a slight lag between the attainment of maximum pressure and the apparent onset of the *maximum* rate of cooling. This delay suggests that the whole of the charge had not been burnt when the maximum pressure was reached. The unburnt residue appeared to be about 1 part in 500 in the first series of explosions (without the cage) and about half that amount in the second and to be of the same order of magnitude through a series of "Matched Explosions".

It may be noticed that the small addition of hydrogen—to which reference has already been made—has been omitted from the expressions representing the composition of the mixtures at T_m. This has been done for simplicity, as the inclusion of hydrogen would have added four terms to the left-hand side of the equations and three to the right, as will be gathered from the example given in § 1 of Appendix I.

The "Matched Explosion" experiments can be divided into four main series, in accordance with the temperature ranges covered. Series 1 relates to the temperature range 100–2100° C; series 2, 100–2380° C; series 3, 100–2660° C; and series 4, 100–2790° C; the results being given in Tables II–V. The tables give, in general, the measured values of the initial pressure and temperature, the maximum pressure and the explosion time for each experiment, together with the conventional maximum temperature T_e computed from these data. The temperature $T_{1/10}$ calculated from the explosion record for the point 0·1 sec. after the attainment of the maximum pressure is given for the experiments in which the cage was *not* employed. The correction to the without-cage maximum temperature due to equalization of the temperature gradient is also given. The quantities on the right-hand side of the tables relate to the composition of the gas mixture under various temperature conditions, namely, at the initial temperature T_i (before combustion), at T_e, $T_{1/10}$ and the gradient corrected temperature of the without-cage experiments, and at T_e with the cage, the values being arranged vertically in this order. Below this are given in each case the initial composition of the mixture selected for gradient calculations and its composition at the without-cage T_e. All compositions are given in g.-mol. per 100 g.-mol. of original mixture.

As the object of the experiments was to obtain the molecular heat of carbon monoxide, nitrogen and carbon dioxide in terms of argon, at least four mixtures were required in each series. Series 2 and 3 complied with this minimum requirement, but in the case of series 1 and 4 additional experiments were made. Thus in series 1 extra experiments were carried out to explore the effect of varying the explosion time and also the concentration of carbon dioxide in the original mixture, and in series 4 the additional experiments were again concerned with a variation in the explosion time. Analyses of all the experimental results were made on the basis of the conventional explosion temperature, and in all but a few the requisite calculations were carried out for converting the conventional explosion temperature into the corresponding uniform gas temperature.

It will, of course, be realized that many more mixtures were made up and exploded than those recorded in the tables—for the matching process involved explosions of trial mixtures before the matching requirements were fulfilled. As to the fulfilment of those requirements, the divergence in the explosion temperatures and in the heat losses in 0·1 sec. in a given series of experiments (see Tables II–VI) may suggest that the matching process was somewhat difficult. That, however, was not the case, the divergences being attributable to the inadequacy of the data on which the preliminary calculations of the explosion temperatures, etc. were based.

In carrying out a series of experiments the argon mixture was made up first and used as the "standard mixture". Explosions of this mixture were usually limited to two and were made at an initial pressure of about 5 atm. in the explosion vessel without the "cage".

The other mixtures were then made up in turn to match the argon mixture, and as the quantity of these mixtures was less restricted than in the case of argon, the usual practice was to carry out two explosions without the cage and two with the cage. As will be observed from Tables II–V, a third explosion was occasionally performed. For example, in the argon mixture S 62*b* of series 2, Table III, the third explosion was performed after the explosions on the other mixtures—without the cage—had been completed. The agreement shown in this case between the explosions of the standard mixture at the beginning and end of the series was very satisfactory.

In the case of the carbon monoxide mixture (S 63*a*) of the same series, the third explosion (without the cage) was carried out after the two explosions with the cage—the agreement again being good. On the other hand, the additional explosion of mixture S 56*d*, series 1, Table II, was due to the agreement between the first two being not quite so close as was desired. The same applies to the argon mixture S 59*b* of the same series. It will be observed, however, that on the whole the agreement between explosions of the same mixture under the same conditions is good.

The molecular heat determinations are based on those experiments for which the gradient correction has been computed, and it is with these results that it is now proposed to deal.

The values obtained for the mean molecular heats of carbon dioxide, carbon monoxide and nitrogen are plotted in fig. 13. For comparison there have been added to fig. 13 certain values based on spectroscopic data and given in Table I, and it will, at once, be seen that the divergence between these two sets of results obtained by such fundamentally different methods is comparatively slight. The present experimental results are certainly much more scattered than the spectroscopic, but this is to be expected, for even with so large an argon content as 50 %, experimental errors are multiplied some threefold or more. In putting curves through the experimental results their shape has been largely dictated by the form of the spectroscopic curves and by the spectroscopic value at 100° C, and although the experimental curves tend to be somewhat higher and steeper than the spectroscopic, the difference is comparatively small.

As to individual results, the only one that would have been affected by the extension of the gradient correction calculations is the nitrogen value in the first series. It is probable that the additional argon and nitrogen mixtures, S 59*b* and S 60*f* of Table II, would give a C_{N_2} value about 2 % higher than that deduced from mixtures S 54*c* and S 56*d*.

The most interesting feature of these "Matched Explosion" experiments is that the possibility of basing the results on the constancy of the specific heat of argon was seemingly inadmissible until the analysis had been carried to the elaborate stage that was ultimately reached.

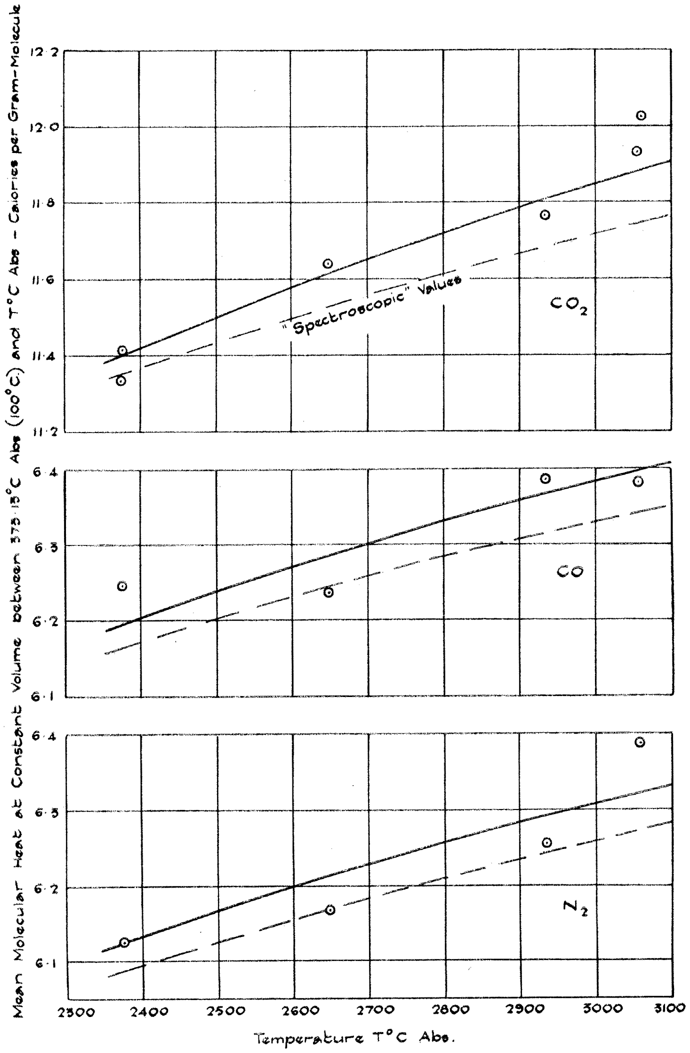

FIG. 13. Experimental values of mean molecular heat at constant volume.

The preparation of this report was commenced on the basis of the conventional explosion temperature and of determinations of the mixture composition at that temperature which took account of the major dissociations but neglected the formation of OH, atomic hydrogen, atomic oxygen and atomic nitrogen. As the quantity of hydrogen in the original mixtures was small (see Tables II–V), it was assumed that it would be unnecessary to consider any other reaction than the formation of water vapour. The results obtained on this basis are given in the curves marked *A* in fig. 14, which show that in all three gases, carbon monoxide, nitrogen and carbon dioxide, the mean molecular heat, *in terms of that of argon*, drops off as the temperature rises, and hence if the molecular heat of argon is constant, the molecular heats of the gases named decrease with increase in temperature. This was seen to be at variance not only with explosion results obtained by other investigators and with computations based on spectroscopic data, but with the results given by the experiments themselves when analysed without regard to argon as a standard of reference. Thus, by abandoning the theory of the constancy of the specific heat of argon, and solving equations (i) to (iv) on p. 175 by the use of values of *P* found or deduced from heat loss measurements given by the "cage" (see p. 182), much more reasonable values were obtained for the molecular heats of carbon monoxide, nitrogen and carbon dioxide, but the molecular heat of

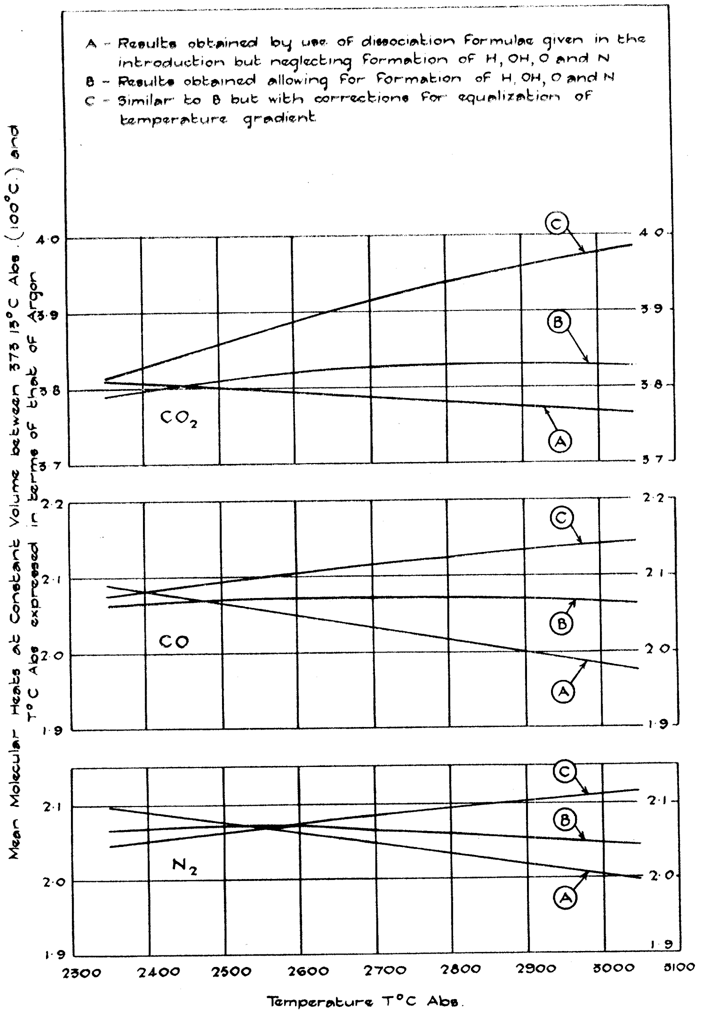

FIG. 14. Influence of method of analysis on values obtained for the mean molecular heat at constant volume.

argon was found to increase rapidly with increase in temperature. The curves marked *A* in fig. 15 indicate the results obtained by this process. At this stage of the analysis, therefore, there seemed to be some grounds for questioning the constancy of the specific heat of argon, although the likelihood of that being accepted seemed to be somewhat remote.

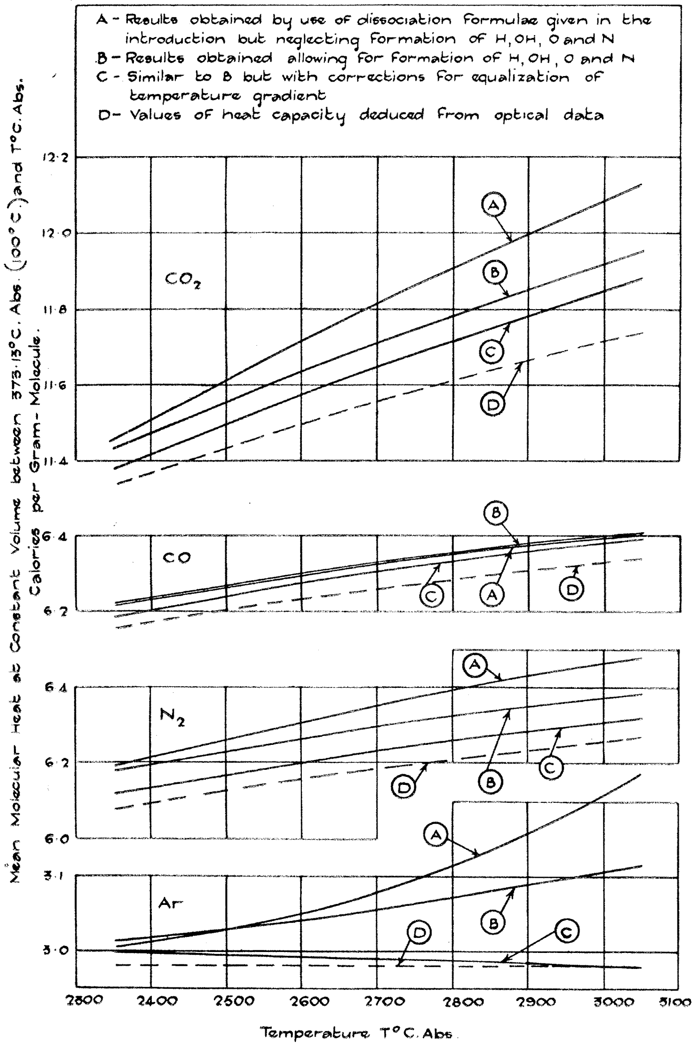

FIG. 15. Influence of method of analysis on values obtained for the molecular heats at constant volume.

The realization that the results so far obtained might have been adversely affected by the failure to take account of the formation of OH, atomic hydrogen, atomic oxygen and atomic nitrogen—even though the hydrogen concentration in the unburnt mixture was low—led to a redetermination of the mixture compositions at the explosion temperature so as to satisfy all the equations given on p. 150.

This in turn led to an appreciable modification of the molecular heats of carbon monoxide, nitrogen and carbon dioxide in terms of argon (see curves marked *B* of fig. 14), the curves becoming practically horizontal. It was still difficult, however, to interpret these results on the basis of a constant specific heat for argon, especially when the simultaneous solution based on "cage" heat losses gave the results illustrated by curves marked B in fig. 15.

A comparison of curves A and B of figs. 14 and 15 shows that although the more thorough analyses had improved the position, it had by no means removed the doubt as to the constancy of the specific heat of argon.

A further explanation was sought and this led to consideration being given to the effect of the temperature gradient in the gas mixture at the maximum explosion pressure. A preliminary study some years earlier had indicated that the gradient might be very pronounced, and this had suggested that in view of the rapid change in dissociation with change in temperature the effect might be very substantial. This, however, was not supported by Lewis and von Elbe who went into the matter much more thoroughly (1934*c*) and came to the conclusion that in certain mixtures the smoothing out of the gradient—without loss of internal energy—would cause a rise of the explosion pressure of less than 1 %. A closer study of their work showed that although these corrections were small they tended to group themselves according to mixture composition, and the fact that they were highest where argon was concerned seemed to be sufficiently significant to justify the calculation of similar corrections in the case of the fourth series of the "Matched Explosions". These calculations were made by the method already indicated, and it was found that the corrections varied sufficiently with the type of mixture to make the simultaneous solution of the corrected equations—based on "cage" heat losses—yield an argon molecular heat value of just under 2·98.

This was followed by the calculation of gradient corrections for nearly all the mixtures of the other three series with equally satisfactory results. On applying these corrections, the molecular heats of carbon monoxide, nitrogen and carbon dioxide in terms of argon were found to increase with temperature as shown by the curves marked C in fig. 14. Further, the simultaneous solution of the corrected equations—based on "cage" heat losses—gave the curves marked C in fig. 15, from which it will be seen that instead of the specific heat of argon rising with temperature it tends to fall slightly. The values obtained for argon were, however, reasonably close to the theoretical value, and any departure may be attributed to errors in the "cage" measurements of the heat loss.

Having disposed of the evidence of any lack of constancy of the specific heat of argon, the final analysis of the experimental results was made in accordance with the original plan, for it was now permissible to take the theoretical value of the specific heat of argon and *base results entirely upon it*, the cage heat losses being used merely as an interesting check. The results of such an analysis have already been given.

Adverting to these results as given by the curves in fig. 13 and the corresponding equations of these curves given later (see Summary, p. 202), it cannot be claimed that the comparatively small difference between the present explosion results and the spectroscopic values should be given any weight so far as the diatomic gases carbon monoxide and nitrogen are concerned. In the case of carbon dioxide, it might be permissible to draw the conclusion that possibly the spectroscopic values for this gas are a little low in the high-temperature region.

In order to demonstrate the satisfactory manner in which the spectroscopic values of the mean molecular heats, as given in Table I, fit into the present experiments, the heat capacities of the various mixtures at the corrected explosion temperatures have been worked out on these molecular heat values and compared with the heat attributable to the chemical reactions. The difference represents the quantity of heat unaccounted for and *includes* that lost to the explosion vessel walls. From the results of these calculations, as given in the last column of Table VI, it will be seen that the heat unaccounted for is of a comparatively small order of magnitude and might well represent the heat absorbed by the explosion vessel walls. The values of this latter quantity as computed for the present experiments both directly (see last column but one) and by means of the "cage" are given for comparison.

Lewis and von Elbe (1935 *b*) applied a similar method in the examination of the results of explosions of mixtures consisting of hydrogen and oxygen and some diluent, and in the majority of cases they found that the balance left no margin for heat loss. In any case agreement within the comparatively small heat-loss margin must be considered as decidedly satisfactory. The hydrogen experiments in the present investigation are dealt with later (see p. 185), but before passing on to these it is of interest to refer to the two explosions of series 1 (Table II) in which the carbon dioxide content was varied. Thus, in mixture S 57 *c*, the carbon dioxide concentration in the original mixture was 33·64 mol. and the carbon dioxide formed on combustion was 24·906 mol. In S 58 *e*, on the other hand, the original carbon dioxide content was 20·236 mol. and the carbon dioxide formed 23·036 mol. The value of the molecular heat of carbon dioxide as determined from S 57 *c* was, however, slightly higher than the value given by S 58 *e*, thus suggesting that the heat capacity of the newly formed carbon dioxide is somewhat *less* than the "stabilized" gas. It is considered, however, that this difference is no more than an experimental discrepancy, but it is desired to point out that these particular experiments give no support to the theory advanced in some quarters (David and Davies 1930) that the freshly formed gas has a *higher* energy content than the ordinary carbon dioxide.

(*d*) *Heat loss measurements as given by the "cage"*. Although the heat-loss measurements as given by the "cage" were not required in the final determination of the molecular heats of carbon monoxide, nitrogen and carbon dioxide (fig. 13) that have just been discussed, they are needed in connexion with the subsequent experiments on the molecular heats of hydrogen and water vapour, and hence some consideration must be given to their significance.

The insertion of the cage increases the effective area of the cooling surface of the explosion vessel by some 50 % and causes a depression in the conventional explosion temperature. If the cage surface formed a true extension of the vessel wall surface, then

Table VI. Measured and calculated heat losses in "matched explosions"

Mixture no.	Initial press. atm.	Corrected max. temp. T_m ° C abs.	Explosion time sec.	Decrease in explosion temp. due to "cage" ° C	Reaction heat at T_m per 100 mol. of original mixture (A) kcal.	Heat capacity of combustion products between T_i and T_m based on "spectroscopic" mean C_v's per 100 mol. of original mixture (B) kcal.	Heat loss* during 0·1 sec. after maximum pressure	Heat loss during explosion period expressed as a percentage of the reaction heat at T_m				
								Values deduced from "cage" exps.			Values given by difference between (A) and heat capacity calculated by use of mean C_v's read off figs. 13 and 16	Loss based on "spectroscopic" C_v data: $\frac{(A)-(B)}{(A)}$
								Uncorrected (C)	Fully corrected (D)	Mean of (C) and (D)		
S 54*c*	5·023	2376	0·106	—	942·3	918·9	7·7	—	—	—	2·2	2·5
S 55*n*	3·686	2372	0·106	—	1355·8	1316·3	7·6	—	—	—	2·5	2·9
S 56*d*	3·608	2378	0·103	—	1347·0	1310·6	7·8	—	—	—	2·2	2·7
S 57*c*	3·131	2365	0·106	—	1724·3	1677·4	7·9	—	—	—	2·3	2·7
S 58*e*	3·288	2366	0·106	—	1571·7	1533·0	7·8	—	—	—	2·0	2·5
S 62*b*	4·997	2648	0·079	—	1120·4	1094·5	8·9	—	—	—	1·9	2·3
S 63*a*	4·725	2639	0·082	20	1561·3	1526·8	8·4	2·0	0·8	1·4	1·5	2·2
S 64*d*	4·154	2635	0·079	19	1883·8	1835·1	8·6	2·0	0·6	1·3	1·9	2·6
S 65*c*	4·632	2645	0·078	19	1556·4	1521·4	8·6	1·9	0·8	1·3	1·6	2·2
S 67*a*	4·995	2933	0·059	—	1308·4	1280·9	10·9	—	—	—	1·4	2·1
S 68*d*	4·983	2938	0·059	19	1813·6	1772·3	9·8	1·8	0·7	1·2	1·4	2·3
S 69*d*	4·618	2906	0·060	15	2093·7	2047·4	10·3	1·9	0·6	1·3	1·3	2·2
S 70*c*	3·722	2918	0·059	17	1787·7	1745·8	12·4	2·3	0·9	1·6	1·5	2·3
S 71*b*	4·995	3056	0·049	—	1404·1	1373·2	13·9	—	—	—	1·5	2·2
S 72*f*	4·254	3037	0·048	10	2273·0	2209·8	15·1	2·3	0·5	1·4	1·7	2·8
S 73*c*	4·478	3045	0·050	12	1906·8	1854·8	14·0	2·2	0·8	1·5	1·8	2·7
S 74*c*	3·069	3065	0·047	23	1925·5	1879·9	13·9	2·5	1·2	1·8	1·4	2·4
S 71*a*	4·993	3062	0·072	—	1415·5	1377·5	12·7	—	—	—	1·9	2·7
S 72*c*	4·249	3035	0·073	14	2294·4	2213·0	13·8	3·0	1·0	2·0	2·5	3·5

* The heat loss during 0·1 sec. after the attainment of the maximum pressure is expressed as a percentage of the heat capacity of the products of combustion between T_i and the conventional maximum temperature, the calculation being based on "spectroscopic" mean C_v's.

this temperature drop, converted into loss of internal energy and multiplied by two, should give a slight underestimate of the loss of heat to the walls of the explosion vessel during the explosion time. The underestimation is due to the explosion temperature being somewhat lower in the explosions with the cage than in those without and a correction can be introduced to allow for this effect.

This, however, is not the only correction that must be applied, for the projection of the cage surface into the explosion vessel may involve serious errors. The effect of this projection is twofold; it makes the cage surface ineffective in regard to the absorption of radiation in the earlier stages of flame propagation but too effective in absorbing heat by conduction in the later stages, for the cage is enveloped or partially enveloped in flame for an appreciable time before the flame reaches the explosion vessel walls. Although these effects act in opposite directions, the second is likely to be very much the greater since, with the polished surfaces used, the radiation losses are probably small.

A correction for the heat loss due to the immersion of the cage in the flame can be obtained from the normal rate of cooling *after* the flame reaches the walls if the time of immersion is known. The mean distance of the cage surface from the walls is about 1/24th of the radius of the vessel and, at first, this requisite time interval was taken as that fraction of the explosion time. A study of Lewis and von Elbe's flame velocity analysis (1934*a*) did not, however, justify this uniform (relative to vessel) flame velocity assumption, and it seemed more reasonable to work on a pressure basis and to consider that the development of 60 % of the total pressure rise coincided with the flame having travelled 23/24ths of the radius, the time for the development of the last 40 % of the pressure rise being obtainable from the explosion-time record. The correction based on this time interval and the appropriate cooling rate was of considerable magnitude, being about two-thirds of the figure to be corrected. As the corrections in the opposite sense were comparatively small, the fully corrected figure for the heat loss was about one-third of the uncorrected. As a compromise it was decided to take a mean of the fully corrected and uncorrected figures as representing the heat loss, and it will be seen from the curves marked *C* in fig. 15 that the use of this figure for the heat loss gives an argon molecular heat sufficiently close to 2·98 to indicate that it is reasonable.

It should be emphasized that the molecular heat determinations of fig. 13 are independent of any heat-loss measurements. Heat losses can, however, be deduced from them by taking the difference between the heat of reaction and the heat accounted for in the gas mixture. Such deduced losses support the mean cage figure (see Table VI, columns 11 and 12) and give some sanction for its use in connexion with the hydrogen and water-vapour experiments which follow.

Before passing on to these experiments it should be made clear that, apart from the magnitude of the corrections that have to be applied, the "cage" is by no means an ideal device for measuring heat loss. It will be observed that its measurements are based on the difference between two pressures of nearly the same magnitude, those reached in explosions with and without the cage. This difference may be as small as $\frac{1}{2}$ % or less and hence the pressures from which it is derived must be measurable with precision and "repeatable" with great consistency. Under favourable conditions, the temperatures in two explosions of the same mixture agree within say 2°, i.e. 0·1 % or less, but even this degree of "repeatability" permits a wide margin of error in a $\frac{1}{2}$ % difference. Further, its deficiencies as a means of measuring the heat loss are not compensated by any ability to reveal whether the presence of a "cold" surface delays the combustion of the boundary layer of the mixture, for a delay at the wall surface will be almost coincident with the attainment of maximum pressure and may affect that pressure considerably, whereas similar delays at the cage surface occur considerably before the maximum pressure and will probably be of insufficient duration to affect it.

It may also be argued that the temperature drop due to the cage—and the resulting loss of internal energy—is based on a comparatively small drop throughout the whole mixture, whereas the actual drop is probably enormously greater but confined to a comparatively small portion of the whole charge. This conventional treatment is, however, allowable provided the final result can be checked against some independent calculation of heat loss, but it will be observed that the latter also suffers from being a small difference between a large heat of reaction and a large heat capacity.

In practice the cage was found to give reasonably consistent results, indicating that in careful experimental work it may play a useful part. The mean of the uncorrected and fully corrected figures is taken as the heat loss.

(*e*) *Explosions for the determination of the molecular heat of* H_2 *and* H_2O. When considering this section of the investigation—a section which involves the explosion of mixtures containing a considerable quantity of hydrogen—there appeared to be no simple means of equalizing the explosion times of the mixtures to be compared, and hence the method of balanced heat losses could not be applied. Experience gained from earlier experiments in this investigation had also shown that it was difficult to deduce heat losses from explosions carried out on the same mixture at different densities, and hence it was decided to employ the "cage" for obtaining a figure for the heat loss. This method has already been discussed at some length (see pp. 182–5).

It is well known that hydrogen explosions differ widely from carbon monoxide explosions in the rate of flame propagation. In the carbon monoxide explosions a small quantity of hydrogen had to be added to speed up the combustion, whereas in the hydrogen explosions steps had to be taken to decrease its rapidity and so permit satisfactory explosion records being obtained. A rapid rate of pressure rise sets up a ripple on the pressure-time record (see record 519 of fig. 18), the frequency being that of the mechanism for magnifying the deflexion of the diaphragm, namely, about 1100 per sec. The amplitude of the ripple increases with decrease in explosion time and with increase in the initial pressure of the charge. When the ripple is clearly defined there is no difficulty in getting its mean height, and it is the mean of the half ripple following the peak that is taken as the maximum pressure, although this may be a slight underestimate. On some occasions, however, the later stages of the combustion seem to be accompanied by a shock which imparts a sideways component to the ripple and spoils its definition. Measurements are still possible, but they lack the precision necessary for work of this type where an error may be multiplied two or three times in the final result.

In explosions of mixtures of hydrogen and oxygen satisfactory explosion records can be obtained provided the ratio of hydrogen to oxygen is large and hence the explosion temperature comparatively low. At lower ratios and higher temperatures the shock effect precludes the further use of such gas mixtures, and in order to surmount this difficulty nitrous oxide was used in place of oxygen.

In several of the experiments water vapour formed a considerable constituent of the original mixture, the water vapour being added by the method given in § 2 (*h*), p. 161. Preliminary and subsequent experiments on the evaporation of known masses of water into the explosion vessel by this method gave water-vapour pressures which were some 1–2 % below those that would be expected from data based on work carried out at the Massachusetts Institute of Technology (Keyes and others 1935) (see Appendix II). As a rule the deficiency was greater when the "cage" was present, and this lent support to the possibility of some absorption of water vapour by the vessel walls. Actually the experimental results were worked out on the basis of the weight of water evaporated as well as on the mass of water vapour calculated from pressure, temperature and volume measurements in conjunction with the M.I.T. formula given in Appendix II. The difference in the values obtained for the molecular heats was, however, comparatively small, for the variation in the water vapour content was accompanied by a variation in the computed heat loss and the two effects tended to neutralize one another.

With mixtures containing water vapour, a special technique had to be devised for measuring their compressibility characteristics, for it was no longer possible to employ the method (see Supplement) used for gas mixtures. It was considered that their departure from perfect gas behaviour might be considerable and the method employed to determine its magnitude consisted in the preparation, in the explosion vessel, of a series of known and decreasing masses of the mixture concerned and the measurement of the pressure produced by such masses, the volume being constant. The readings obtained enabled the value of the product pv, for a constant mass under decreasing pressure conditions, to be deduced, and an extrapolation to zero pressure permitted the determination of the required ratio of the pv value under the initial pressure and temperature conditions of the normal explosion experiment to its value when the temperature was the same but the pressure infinitely low. The method did not give results with a high degree of precision, for its accuracy is not likely to exceed 1 part in 1000.

H_2-O_2 *explosions*. As to the experiments carried out for the determination of the molecular heats of hydrogen and water vapour, the most direct were those in which mixtures of the type

$$(2+a)\,H_2+O_2 \quad \text{and} \quad (2+b)\,H_2+O_2+c\,.\,H_2O$$

were exploded and the equations representing their heat capacities at T_m solved simultaneously for C_{H_2} and C_{H_2O}. Except at low oxygen concentrations, however, the rapidity of flame propagation was too great to permit satisfactory recording of the explosion pressure. The device of lowering the initial pressure of the whole charge was used to extend the range as far as possible but, in spite of this, the maximum temperature at which satisfactory records were obtained did not exceed 2235° C (abs.).

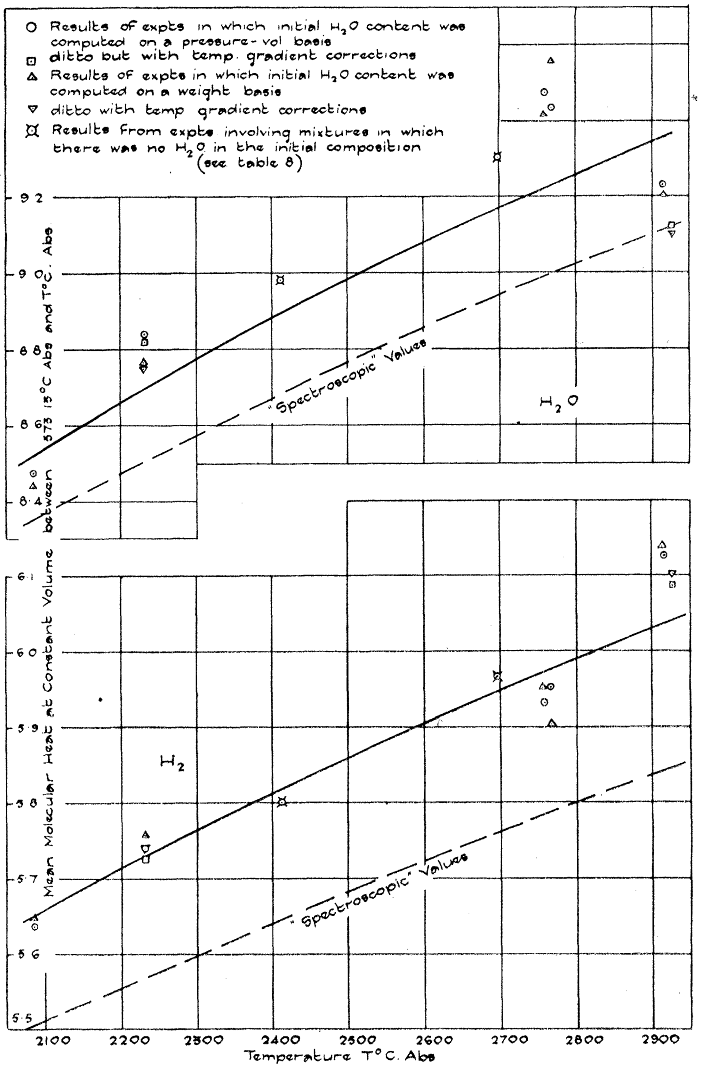

FIG. 16. Mean molecular heat at constant volume of hydrogen and water vapour.

The first pair of mixtures of this type, namely, S 94 and S 95*c* (Table VII), covered the temperature range 373–2085° C (abs.) and gave the values of C_{H_2} and C_{H_2O} that have been plotted in fig. 16. It will be observed that two values have been plotted for each gas, the explanation being that results were worked out on the basis of the two methods for determining the water-vapour content of the unburnt mixture, to which allusion has already been made. The two values thus obtained are in fairly close agree-

TABLE VII. EXPERIMENTAL AND OTHER DATA RELATING TO MIXTURES OF THE TYPE $(2+a)\,H_2+O_2$ AND $(2+b)\,H_2+O_2+c.H_2O$

			Initial conditions							Mixture composition in gram-molecules					
Mixture no.	"PV" ratio	"Cage"	Temp. T_i ° C abs.	Press. P_i atm.	Explosion time sec.	Max. press. from explosion record P_e atm.	Temp. corresponding to P_e T_e ° C abs.	Temp. gradient correction ° C		H_2O (gas)	H_2	H	OH	O_2	N_2
S 94–534	0·9961	No	373·6	3·460	0·0132	17·46	2086	Not calc.	Initially	27·067	62·845	—	—	9·983	0·105
									At $T=2086°$	47·019	42·864	0·045	0·013	—	0·105
S 94–535	0·9961	,,	373·6	3·450	0·0132	17·43	2088	,,	Initially	27·131	62·790	—	—	9·974	0·105
									At $T=2088°$	47·066	42·826	0·045	0·013	—	0·105
S 94–532	0·9961	Yes	373·4	3·448	0·0132	17·10	2049	,,	Initially	27·138	62·783	—	—	9·973	0·106
									At $T=2049°$	47·074	42·824	0·035	0·010	—	0·106
S 94–533	0·9961		373·5	3·452	0·0132	17·08	2045	,,	Initially	27·134	62·787	—	—	9·973	0·106
									At $T=2045°$	47·071	42·828	0·034	0·010	—	0·106
S 95*c*–539	1·0022	No	373·2	3·430	0·0113	17·59	2099	Not calc.	Initially	—	91·211	—	—	8·663	0·126
S 95*c*–540	1·0022	,,	373·3	3·425	0·0113	17·53	2096	,,	At $T=2098°$	17·322	73·855	0·063	0·004	—	0·126
S 95*c*–541	1·0022	Yes	373·3	3·422	0·0113	17·37	2078	,,	At $T=2078°$	17·323	73·859	0·056	0·003	—	0·126
S 95*c*–542	1·0022	,,	373·2	3·430	0·0115	17·41	2078	,,							
S 96–546	0·9962	No	373·7	3·439	0·0095	18·39	2237	3	Initially	27·408	61·425	—	—	11·088	0·079
									At $T=2237°$	49·543	39·220	0·100	0·041	—	0·079
									At $T=2240°$	49·542	39·219	0·101	0·042	—	0·079
S 96–547	0·9962	,,	373·6	3·438	0·0095	18·32	2229	3	Initially	27·434	61·403	—	—	11·084	0·079
									At $T=2232°$	49·563	39·205	0·098	0·040	—	0·079
S 96–544	0·9962	Yes	373·7	3·436	0·0089	18·10	2204	—	Initially	27·384	61·445	—	—	11·092	0·079
S 96–545	0·9962	,,	373·6	3·439	0·0089	18·11	2202	—	At $T=2203°$	49·535	39·236	0·084	0·033	—	0·079
									Gradient mixture:						
									Initially	27·610	61·956	—	—	10·434	—
									At $T=2237°$	48·439	41·056	0·103	0·039	—	—
S 97*b*–549	1·0021	No	373·9	3·434	0·0083	18·52	2232	4	Initially	—	90·376	—	—	9·543	0·081
S 97*b*–550	1·0021	,,	373·9	3·437	0·0081	18·50	2228	4	At $T=2230°$	19·075	71·230	0·130	0·011	—	0·081
S 97*b*–551	1·0021	Yes	373·9	3·437	0·0084	18·38	2213	—	At $T=2234°$	19·075	71·229	0·133	0·012	—	0·081
S 97*b*–552	1·0021	,,	373·9	3·440	0·0083	18·38	2212	—	At $T=2213°$	19·076	71·235	0·119	0·010	—	0·081
									Gradient mixture:						
									Initially	—	90·920	—	—	9·080	—
									At $T=2230°$	18·149	72·699	0·132	0·011	—	—

The water vapour content of the unburnt mixture is based on pressure, temperature and volume readings. The alternative set of results based on the weight of water evaporated is not given.

TABLE VIII. EXPERIMENTAL AND OTHER DATA RELATING TO MIXTURES* OF THE TYPE $(2+b)\,H_2+O_2+2N_2+d.H_2$ AND $(2+b)\,H_2+O_2+2N_2+e.N_2$

Mixture no.	"PV" ratio	"Cage"	Initial conditions		Explosion time sec.	Max. press. from explosion record P_e atm.	Temp. corresponding to P_e T_e ° C abs.		Mixture composition in gram-molecules									
			Temp. T_i ° C abs.	Press. P_i atm.					H_2O (gas)	H_2	H	OH	O_2	O	NO	N_2	N	Ar
S 83	1·0017	No	373·4	2·002	0·0047	12·65	2706	Initially	—	59·777	—	—	13·268	—	—	26·436	—	0·319
		,,	373·2	2·000	0·0048	12·57	2691	At $T=2697°$	26·168	33·189	0·892	0·349	0·0011	0·0032	0·0139	26·427	0·0044	0·319
		,,	373·3	2·002	0·0046	12·60	2694											
		Yes	373·6	2·001	0·0048	12·48	2673	At $T=2676°$	26·201	33·204	0·826	0·318	0·0009	0·0027	0·0123	26·428	0·0039	0·319
		,,	373·6	2·002	0·0047	12·49	2674											
		,,	373·7	2·002	0·0047	12·52	2680											
S 85	1·0029	No	373·8	4·991	0·0066	28·73	2414	Initially	—	67·570	—	—	10·736	—	—	21·436	—	0·258
		,,	373·7	4·993	0·0066	28·73	2413	At $T=2413°$	21·433	46·012	0·212	0·039	—	0·0001	0·0008	21·435	0·0004	0·258
		Yes	373·5	4·984	0·0069	28·54	2400	At $T=2400°$	21·435	46·017	0·200	0·036	—	—	0·0007	21·435	0·0004	0·258
		,,	373·5	4·995	0·0068	28·62	2401											
S 87*b*	1·0025	No	373·3	4·990	0·0112	28·67	2410	Initially	—	32·650	—	—	10·874	—	—	56·218	—	0·258
		,,	373·2	4·989	0·0117	28·64	2407	At $T=2409°$	21·664	10·897	0·101	0·078	0·0002	0·0002	0·0054	56·215	0·0006	0·258
		Yes	373·7	4·991	0·0116	28·50	2398	At $T=2398°$	21·669	10·896	0·096	0·073	0·0002	0·0002	0·0051	56·215	0·0006	0·258
		,,	373·7	4·990	0·0117	28·46	2395											
		,,	373·6	4·991	0·0115	28·50	2398											
			373·6	4·991	0·0118	28·52	2399											

* No temperature gradient calculations were made for these mixtures.

ment, and it is not considered necessary to duplicate Table VII in order to show in detail the comparatively small variations involved when the water-vapour content is taken as the weight of water evaporated. It should be noted that temperature-gradient corrections were not computed for this pair of mixtures; but their magnitude is likely to be insignificant.

Owing to the limitations imposed by "knock" there was only one other pair of mixtures of this type, namely, S 96 and S 97*b* of Table VII. In this case a calculation of the temperature-gradient correction was made on the basis of the simplified mixtures given in the same table. The correction proved to be small, between 3 and 4° C, and to be nearly the same for both mixtures.

In plotting the values deduced—from this pair of mixtures—for C_{H_2} and C_{H_2O} over the temperature range 373–2235° C (abs.), a distinction has been made between the values obtained with and without the gradient correction as well as between the values based on the two methods of determining the initial water-vapour content of S 96.

Reference should be made to Table XI for details of the heat losses pertaining to this and the previous pair of mixtures. In conformity with the experience obtained from the "Matched Explosions" the heat loss has been taken as the mean of the uncorrected and corrected values given by the "cage" method, and it will be observed that it is of the order of 3–4 % of the reaction heat in the case of the mixtures diluted with water vapour but about half that quantity in the case of the nominally dry mixtures. It is interesting to note in this connexion that Wohl and von Elbe (1929) found that a small addition of water vapour to a really dry mixture reduced the heat loss.

H_2-O_2-N_2 *explosions.* When nitrogen is added to reduce the rate of flame propagation, satisfactory explosion records can be obtained from hydrogen-oxygen mixtures giving explosion temperatures about 200° higher than the previous limit. Thus two mixtures, S 85 and S 87*b* of Table VIII, of the type

$$(2+b)\,H_2+O_2+2N_2+d.H_2 \quad \text{and} \quad (2+b)\,H_2+O_2+2N_2+e.N_2,$$

were found by experiment, which gave practically the same explosion temperature. The solution of the heat capacity equations of their high temperature products gives the ratio of the molecular heat of hydrogen to that of nitrogen. In this particular case the ratio was $C_{H_2} : C_{N_2} :: 0{\cdot}945 : 1$, the temperature range being 373–2413° C (abs.) and the heat losses those determined by the cage (see Table XI). If use is made of the value already obtained for C_{N_2}, namely 6·138 (see fig. 13), then $C_{H_2} = 5{\cdot}801$ and $C_{H_2O} = 8{\cdot}98$. These values have been plotted in fig. 16: they have the drawback of being dependent on C_{N_2}.

H_2-N_2O *explosions.* An exploration was made of the possibility of obtaining the molecular heat of hydrogen from the comparison of mixtures of the type

$$(2+a)\,H_2+2N_2O \quad \text{and} \quad (2+c)\,H_2+O_2+2N_2,$$

but it was found that at least 22 % of nitrous oxide was required to produce an explosive mixture and this gave an explosion temperature of 2750° C (abs.), whereas the occurrence of "knock" in the oxygen mixtures made this temperature the highest at which satisfactory records were obtained, those at the higher temperature of 2930° C (abs.) having to be discarded.

Thus the two series of experiments overlapped at one temperature only, but in view of the subsequent use to which the hydrogen-nitrous oxide experiments were put it is appropriate to deal with them at this stage. The series consisted of four mixtures with increasing concentrations of nitrous oxide, the lowest concentration being much greater than had been anticipated. The initial pressure was about $4\frac{1}{2}$ atm. throughout and the initial temperature 100° C, and these and other details are given in Table IX, the conventional explosion temperature and the explosion time being shown graphically in fig. 17.

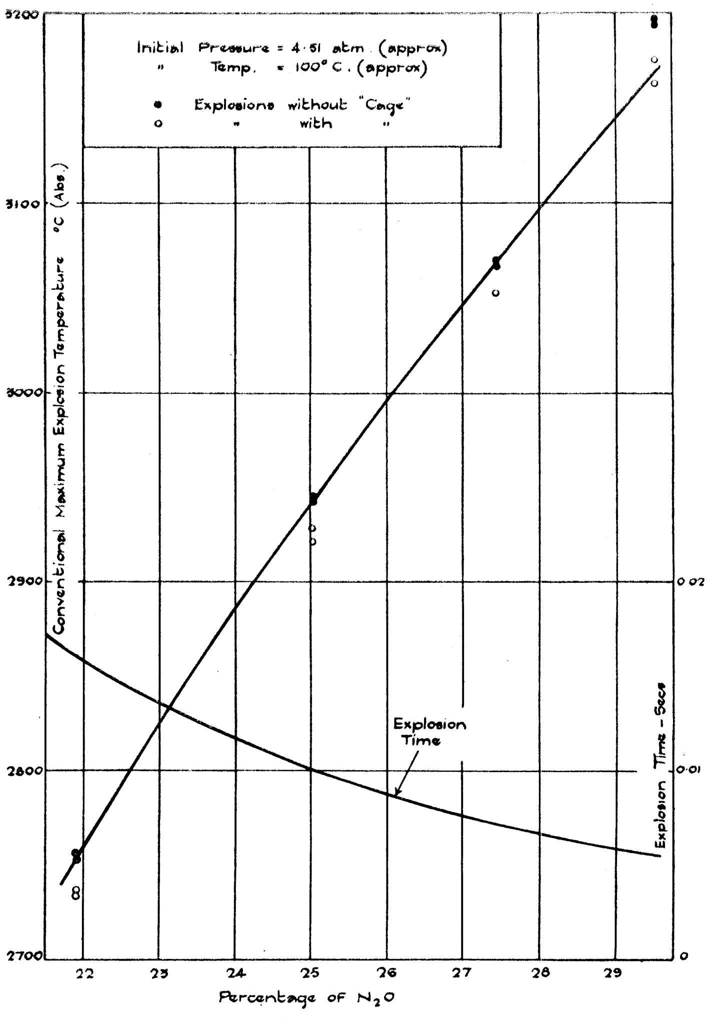

FIG. 17. Explosion of mixture of the type $(2+a)\ H_2 + 2N_2O$ (see Table IX).

The explosions giving the highest temperature, nearly 3200° C (abs.), are probably unreliable owing to "knock", and hence the shape of the maximum temperature curve in fig. 17 has been dictated by the other three points. "Knock" is much less in evidence in hydrogen-nitrous oxide explosions than in those of hydrogen and oxygen, and this series was satisfactory in that respect with the exception of the highest temperature mixture. To be able to obtain satisfactory explosion records at temperatures of 3000° C (abs.) or somewhat higher is a marked advance on hydrogen-oxygen experience. As to the parallel series of explosions the mechanical addition of nitrogen to oxygen was much less effective in suppressing "knock" than the chemical combination of those gases. Thus mixture S 83 of Table VIII, in which the proportion of nitrogen to oxygen was 2 to 1, gave too "violent" an explosion at an initial pressure of 3 atm. The initial pressure was reduced to 2 atm., at which the explosion record was more or less satisfactory and the maximum temperature just under 2700° C (abs.). This temperature is about 50° below the lowest temperature pertaining to the hydrogen-nitrous oxide series, but the composition of the corresponding mixture can be obtained by extrapolation. An alternative to extrapolation is the reduction of the experimental value of the heat capacity of the products of the hydrogen-nitrous oxide mixture between 373 and 2750° C (abs.) to the range 373–2700° C (abs.) on the basis that the change is proportional to that associated with the spectroscopic values of the molecular heat given in Table I. Computing results by both methods and taking the mean, a figure of about 5·97 is obtained for the mean molecular heat of hydrogen over the temperature range 373–2697° C (abs.). The nitrogen in the heat-capacity equations can be eliminated by inserting its value from fig. 13, and if this is done the mean molecular heat of water vapour over the same range is found to be 9·30. These figures should not be taken as they stand but must be related to the other experiments by the curve shown in fig. 16.

Owing to the failure, already mentioned, of the H_2-N_2O and the H_2-O_2-N_2 series to provide the requisite data *over the same temperature ranges*, the result just given is the only one obtained from their comparison.

With a view to reaching higher temperatures and yet avoiding knock, experiments were carried out on mixtures of the type

$$\text{(i)}\quad (2+b)\,H_2+2N_2O+c\,.\,H_2O+c\,.\,N_2,$$

and

$$\text{(ii)}\quad (2+d)\,H_2+2N_2O+e\,.\,H_2O.$$

A comparison of the first series with explosions already made on $(2+a)\,H_2+2N_2O$ gives the molecular heat of hydrogen, whereas a similar comparison in the case of the second series furnishes a value of the ratio of the molecular heat of water vapour to that of hydrogen. In both cases the substitution of a numerical value for the molecular heat of nitrogen makes possible a simultaneous solution for C_{H_2} and C_{H_2O}. On the other hand, the three series can be taken together and their heat capacity equations solved simultaneously for C_{H_2}, C_{H_2O} and C_{N_2}.

Mixtures S 90 and S 91 of Table X represent the first series and S 92 and S 93 of the same table the second. Of these S 93 is under suspicion owing to the occurrence of slight "knock". This in itself is interesting, for here is a case in which the substitution of water vapour for hydrogen in a hydrogen-nitrous oxide mixture seems to give rise to some departure from the normal progressive combustion, despite the fact that the lower initial pressure and explosion temperature of S 93 (Table X) compared with S 82 (Table IX) should have the reverse effect.

As to the results obtained from these series, the simultaneous solution of the heat capacity equations for S 79 (Table IX) and S 90 and 92 (Table X) gives the following values of the mean molecular heats over the temperature range 373–2759° C (abs.): $C_{H_2} = 5{\cdot}93$, $C_{H_2O} = 9{\cdot}40$ and $C_{N_2} = 6{\cdot}32$. The value of C_{N_2} is considerably higher than that obtained from the curve of fig. 13, namely 6·25, and as gradient corrections have not been computed for the mixtures under consideration it is not possible to say how much of the discrepancy is attributable to this. In the circumstances it seems to be preferable to solve the equations in pairs and substitute 6·25 for C_{N_2} where that is necessary. Working on these lines S 79 and S 90 give $C_{H_2} = 5{\cdot}93$, a value which is independent of C_{N_2}, and a figure of 9·47 is obtained for C_{H_2O}. From the pair of mixtures S 79 and S 92 the ratio $C_{H_2O} : C_{H_2}$ is found to be $1{\cdot}58_5 : 1$ and is independent of C_{N_2}. Substituting 6·25 for C_{N_2} in the heat-capacity equations and solving for C_{H_2} and C_{H_2O} it is found that $C_{H_2} = 5{\cdot}95$ and $C_{H_2O} = 9{\cdot}43$. The values of C_{H_2} and C_{H_2O} plotted in fig. 16 are those obtained from this solution in pairs. Figures have been calculated in a similar manner for mixtures in which the original water-vapour content is based on the weight of water evaporated and these have been plotted also.

Coming to a higher temperature, mixtures S 80 (Table IX) and S 91 and 93 (Table X) can be solved simultaneously to give C_{H_2}, C_{H_2O} and C_{N_2}, the values obtained being 6·15, 9·06 and 6·47 respectively for the temperature range 373–2944° C (abs.). The C_{H_2} value is independent of S 93 and can be accepted, but the other values involve this mixture and are therefore in doubt owing to the "knock" which affected the explosion records. Incidentally it will be observed that the C_{N_2} value of 6·47 is nearly 3 % above the curve value of fig. 13, and this high value partly accounts for the low value of C_{H_2O}. Neglecting individual heat capacities, the heat capacity of the mixture as a whole complies with the molecular heat curves of figs. 13 and 16 within about $1\frac{1}{4}$ %, but the individual discrepancies appear to render it useless for solution with the other two.

The solution of S 80—or a mixture containing somewhat less N_2O—and S 91 gives a C_{H_2} value of 6·13 for the temperature range 373–2916° C (abs.). Taking C_{N_2} as having the fig. 13 curve value of 6·29, C_{H_2O} becomes equal to 9·23 for the same temperature range.

In the case of this pair of mixtures, temperature gradient corrections have been worked out; they amount to 10·6° C for the hydrogen-nitrous oxide mixture (see Table IX) and 9·4° C for S 91 (see Table X). Applying these corrections, the temperature range becomes 373–2926° C (abs.) and $C_{H_2} = 6{\cdot}08_5$ and $C_{H_2O} = 9{\cdot}12_5$. The values, both with and without the correction, have been plotted in fig. 16, and in addition the parallel set based on the weight determination of the water-vapour content of the unburnt mixture.

TABLE IX. EXPERIMENTAL AND OTHER DATA RELATING TO MIXTURES OF THE TYPE $(2+a)\,H_2+2N_2O$

Mixture no.	"PV" ratio	"Cage"	Initial conditions		Explosion time sec.	Max. press. from explosion record P_e atm.	Temp. corresponding to P_e T_e °C abs.	Temp. gradient correction °C		Mixture composition in gram-molecules									
			Temp. T_i °C abs.	Press. P_i atm.						H_2O (gas)	H_2	H	OH	N_2O	O_2	O	NO	N_2	N
S 79	1·0022	No	373·6	4·502	0·0160	33·29	2753	Not calc.	Initially	—	77·920	—	—	21·910	—	—	—	0·170	—
		,,	373·4	4·502	0·0160	33·35	2756		At $T=2755°$	21·712	55·642	0·941	0·190	—	0·0002	0·0011	0·0057	22·075	0·0037
		Yes	373·5	4·506	0·0158	33·10	2735		At $T=2737°$	21·727	55·662	0·884	0·177	—	0·0002	0·0010	0·0051	22·076	0·0033
		,,	373·5	4·504	0·0158	33·12	2738												
S 80	1·0017	No	373·2	4·508	0·0099	35·87	2943	Not calc.	Initially	—	74·812	—	—	25·023	—	—	—	0·165	—
		,,	373·2	4·508	0·0101	35·89	2944		At $T=2944°$	24·519	49·244	1·621	0·477	—	0·0011	0·0055	0·0196	25·173	0·0106
		Yes	373·1	4·507	0·0097	35·66	2928		At $T=2924°$	24·553	49·271	1·531	0·445	—	0·0010	0·0048	0·0180	25·174	0·0096
		,,	373·0	4·511	0·0098	35·61	2921												
S 82	1·0015	No	373·6	4·514	0·0073	37·62	3070	Not calc.	Initially	—	72·409	—	—	27·431	—	—	—	0·160	—
		,,	373·6	4·516	0·0074	37·62	3069		At $T=3070°$	26·523	44·360	2·208	0·843	—	0·0037	0·0147	0·0429	27·560	0·0199
		Yes	373·7	4·514	0·0074	37·39	3054		At $T=3054°$	26·569	44·381	2·117	0·801	—	0·0033	0·0134	0·0402	27·562	0·0186
		,,	373·6	4·514	0·0073	37·40	3054												
S 81*	1·0010	No	373·2	4·509	0·0057	39·45	3196	Not calc.	Initially	—	70·333	—	—	29·512	—	—	—	0·155	—
		,,	373·4	4·510	0·0057	39·46	3197		At $T=3196°$	27·968	40·198	2·934	1·400	—	0·0104	0·0362	0·0864	29·606	0·0355
		Yes	372·9	4·512	0·0060	39·04	3163		At $T=3170°$	28·090	40·224	2·743	1·295	—	0·0090	0·0312	0·0782	29·612	0·0318
		,,	373·7	4·511	0·0058	39·11	3176												
From curve on fig. 17	—	—	—	—	—	—	2916	10·6	Initially	—	75·308	—	—	24·527	—	—	—	0·165	—
									At $T=2916°$	24·086	50·260	1·505	0·418	—	0·0009	0·0044	0·0164	24·679	0·0091
									At $T=2926°$	24·068	50·245	1·555	0·435	—	0·0009	0·0047	0·0172	24·679	0·0096
									Gradient mixture:										
									Initially	—	76·708	—	—	23·292	—	—	—	—	—
									At $T=2916°$	22·884	52·857	1·546	0·388	—	0·0007	0·0039	0·0144	23·280	0·0089

* The temperatures T_e of S 81 are probably too high owing to "knock".

TABLE X. EXPERIMENTAL AND OTHER DATA RELATING TO MIXTURES OF THE TYPE $(2+b)\,H_2+2N_2O+c\,.\,H_2O+c\,.\,N_2$ AND $(2+d)\,H_2+2N_2O+e\,.\,H_2O$

Mixture no.	"PV" ratio	"Cage"	Initial conditions		Explosion time sec.	Max. press. from explosion record P_e atm.	Temp. corresponding to P_e T_e °C abs.	Temp. gradient correction °C		Mixture composition in gram-molecules									
			Temp. T_i °C abs.	Press. P_i atm.						H_2O (gas)	H_2	H	OH	N_2O	O_2	O	NO	N_2	N
S90–500	0·9940	No	373·2	4·035	0·0236	30·16	2756	Not calc.	Initially	18·532	37·937	—	—	24·768	0·088	—	—	18·675	—
									At $T=2756°$	42·559	13·262	0·486	0·810	—	0·0138	0·0102	0·0697	43·405	0·0055
S90–501	0·9940	,,	373·3	4·039	0·0240	30·22	2759	,,	Initially	18·476	37·963	—	—	24·784	0·088	—	—	18·689	—
									At $T=2759°$	42·510	13·274	0·492	0·818	—	0·0140	0·0104	0·0707	43·435	0·0056
S90–502	0·9940	,,	373·3	4·043	0·0236	30·25	2760	,,	Initially	18·488	37·956	—	—	24·782	0·088	—	—	18·686	—
									At $T=2760°$	42·519	13·270	0·491	0·818	—	0·0140	0·0104	0·0706	43·430	0·0056
S90–503	0·9940	Yes	373·4	4·042	0·0240	29·96	2736	,,	Initially	18·655	37·879	—	—	24·730	0·088	—	—	18·648	—
									At $T=2736°$	42·717	13·217	0·453	0·748	—	0·0119	0·0088	0·0630	43·344	0·0049
S90–504	0·9940	,,	373·3	4·041	0·0240	29·95	2735	,,	Initially	18·550	37·928	—	—	24·762	0·088	—	—	18·672	—
									At $T=2735°$	42·648	13·232	0·452	0·745	—	0·0118	0·0087	0·0627	43·400	0·0049
S91–513	0·9965	No	373·3	3·021	0·0142	24·02	2917	9·4	Initially	15·032	42·216	—	—	27·472	0·089	—	—	15·191	—
									At $T=2917°$	40·825	15·123	1·013	1·588	—	0·0416	0·0369	0·1494	42·581	0·0148
									At $T=2926·5°$	40·763	15·146	1·041	1·637	—	0·0440	0·0392	0·1554	42·578	0·0154
S91–514	0·9965	,,	373·5	3·012	0·0148	23·91	2915	9·4	Initially	15·059	42·203	—	—	27·464	0·089	—	—	15·185	—
									At $T=2924·5°$	40·790	15·138	1·037	1·630	—	0·0437	0·0388	0·1545	42·564	0·0153
S91–510	0·9965	Yes	372·9	3·009	0·0152	23·71	2892		Initially	15·173	42·146	—	—	27·426	0·089	—	—	15·166	—
									At $T=2892°$	41·082	15·041	0·935	1·458	—	0·0359	0·0314	0·1342	42·518	0·0128
S91–511	0·9965	,,	372·9	3·011	0·0149	23·68	2886		Initially	15·193	42·135	—	—	27·420	0·089	—	—	15·163	—
									At $T=2886°$	41·131	15·027	0·910	1·430	—	0·0346	0·0303	0·1308	42·511	0·0126
									Gradient mixture:										
									Initially	16·137	41·163	—	—	26·463	—	—	—	16·237	—
									At $T=2916°$	40·765	15·243	1·013	1·571	—	0·0405	0·0363	0·1472	42·619	0·0147
S92–519	0·9942	No	373·5	3·007	0·0186	22·57	2764	Not calc.	Initially	24·917	49·046	—	—	25·970	0·003	—	—	0·064	—
									At $T=2764°$	49·963	23·188	0·765	0·859	—	0·0088	0·0098	0·0437	26·010	0·0052
S92–520	0·9942	,,	373·6	3·012	0·0183	22·65	2769	,,	Initially	24·908	49·052	—	—	25·973	0·003	—	—	0·064	—
									At $T=2769°$	49·937	23·196	0·778	0·877	—	0·0091	0·0101	0·0448	26·012	0·0053
S92–517	0·9942	Yes	373·2	3·001	0·0183	22·36	2743		Initially	24·753	49·154	—	—	26·026	0·003	—	—	0·064	—
									At $T=2743°$	49·937	23·221	0·712	0·786	—	0·0075	0·0083	0·0391	26·068	0·0046
S92–518	0·9942	,,	373·3	3·006	0·0185	22·35	2739		Initially	24·867	49·079	—	—	25·987	0·003	—	—	0·064	—
									At $T=2739°$	50·024	23·184	0·701	0·775	—	0·0073	0·0080	0·0382	26·030	0·0045
*S93–526	0·9952	No	373·6	2·525	0·0125	20·39	2945	Not calc.	Initially	24·010	46·193	—	—	29·724	0·004	—	—	0·069	—
									At $T=2945°$	51·127	17·312	1·284	2·244	—	0·0716	0·0581	0·1693	29·701	0·0154
*S93–527	0·9952	,,	373·6	2·527	0·0123	20·41	2945	,,	Initially	23·997	46·201	—	—	29·729	0·004	—	—	0·069	—
									At $T=2945°$	51·114	17·316	1·288	2·249	—	0·0718	0·0582	0·1697	29·705	0·0154
*S93–524	0·9952	Yes	373·5	2·522	0·0125	20·07	2908		Initially	24·221	46·064	—	—	29·641	0·004	—	—	0·070	—
									At $T=2908°$	51·575	17·143	1·146	1·987	—	0·0580	0·0462	0·1453	29·632	0·0128
*S93–525	0·9952	,,	373·5	2·523	0·0125	20·24	2926		Initially	24·214	46·068	—	—	29·644	0·004	—	—	0·070	—
									At $T=2926°$	51·408	17·208	1·214	2·118	—	0·0649	0·0520	0·1574	29·628	0·0141

* There was evidence of a slight "knock" in these experiments.

N.B. The water-vapour content of the unburnt mixture is based on pressure, temperature and volume readings. The alternative set of results based on the weight of water evaporated is not given.

TABLE XI. MEASURED AND CALCULATED HEAT LOSSES IN HYDROGEN EXPLOSIONS

Mixture no.	Initial pressure atm.	Max. temp. T_m °C abs.	Explosion time sec.	Decrease in explosion temp. due to "cage" °C	Reaction heat at T_m per 100 mol. of original mixture (A) kcal.	Heat capacity of combustion products between T_i and T_m based on "spectroscopic" mean C_v's—per 100 mol. of original mixture (B) kcal.	Heat loss during explosion period expressed as a percentage of the reaction heat at T_m			
							Values deduced from "cage" exps.			Loss based on "spectroscopic" C_v data: $\frac{(A)-(B)}{(A)}$
							Uncorrected (C)	Fully corrected (D)	Mean of (C) and (D)	
*S 79	4·502	2755	0·0160	18	1640·7	1566·1	2·2	1·2	1·7	4·5
*S 80	4·508	2944	0·0100	20	1827·0	1740·6	2·4	1·8	2·1	4·7
*S 82	4·515	3070	0·0073	16	1956·5	1863·8	2·1	1·6	1·9	4·7
Mixture off fig. 17	4·5	2926	—	—	1794·9	1722·4	—	—	2·1	4·0
*S 83	2·001	2697	0·0047	21	1459·9	1380·9	2·8	2·4	2·6	5·4
*S 85	4·992	2413	0·0066	13	1224·6	1179·5	1·5	1·1	1·3	3·7
*S 87*b*	4·990	2409	0·0115	11	1243·3	1208·6	1·3	0·8	1·1	2·8
*S 90–500	4·035	2756	0·0236	20†	1849·2	1751·7	2·6	1·4	2·0	5·3
*S 90–501	4·039	2759	0·0240	20†	1849·5	1754·2				5·2
*S 90–502	4·043	2760	0·0236	20†	1849·3	1754·3				5·1
S 91–513	3·021	2927	0·0142	24†	1963·7	1890·3	3·5	2·4	3·0	3·7
S 91–514	3·012	2925	0·0148	24†	1963·8	1888·3				3·8
*S 92–519	3·007	2764	0·0186	28†	1917·9	1798·6	3·6	1·8	2·7	6·2
*S 92–520	3·012	2769	0·0183	28†	1916·2	1803·4				5·9
*S 93–526	2·525	2945	0·0125	23†	2071·2	1986·7	3·8	2·2	3·0	4·1
*S 93–527	2·527	2945	0·0123	23†	2071·0	1986·8				4·1
*S 94–534	3·460	2086	0·0132	39†	1148·0	1077·8	5·2	3·4	4·3	6·1
*S 94–535	3·450	2088	0·0132	39†	1147·0	1079·6				5·9
S 96–546	3·439	2240	0·0095	31†	1270·8	1196·8	3·9	2·0	2·9	5·8
S 96–547	3·438	2232	0·0095	31†	1270·7	1190·9				6·3
*S 95*c*	3·428	2098	0·0113	20	995·5	953·7	2·6	1·7	2·1	4·2
S 97*b*	3·436	2234	0·0082	17	1092·9	1041·9	2·3	1·3	1·8	4·7

* No temperature gradient calculations were made for these mixtures, therefore the T_m's given are the conventional values, whereas those of the other mixtures are fully corrected for equalization of temperature gradient.

† These values were obtained from the difference between the means of the with and without cage maximum temperatures after adjustment to a common mixture composition.

Reviewing the C_{H_2} and C_{H_2O} results as a whole, it should be emphasized that they are dependent on heat losses determined by means of the cage and that a variation in these loss figures may have a considerable effect. Thus in the case of mixture S 91 (Table X), the depression of the conventional explosion temperature due to the insertion of the cage was about 24° C. If this figure is reduced by about $3\frac{1}{2}$° C, the value obtained for C_{H_2} is increased by just over 1 % and that for C_{H_2O} is decreased by nearly 1·5 %. Hence a comparatively slight alteration in the heat loss in *one* of a pair of corresponding mixtures causes a significant change in the molecular heat values. Bearing this in mind it is not surprising that the experimental points in fig. 16 are somewhat scattered in regard to the curve that has been put through them.

The next point of some importance is the omission from many of the results of the temperature-gradient correction. It has, however, been computed for a pair of mixtures near the beginning and a pair near the end of the temperature range. In these cases the corrections were of approximately the same magnitude and of the same sign for the mixtures forming one pair and they were greater for the pair at the high temperature end. These corrected readings have been given additional weight when drawing the curves through the experimental points, although it cannot be assumed that these individual corrections are representative of those applying to mixtures in their neighbourhood.

The third point that arises is the magnitude of the figure for the heat loss that is obtained when the heat capacity of the high-temperature gas mixture—based on the "spectroscopic" molecular heats of Table I—is subtracted from the heat released by the chemical reactions (see Table XI). This quantity would be expected to be greater than the losses given by the "cage", for the molecular heats based on the latter are greater than these "spectroscopic" values as will be seen from a comparison of the curves in fig. 16. Where, however, a discrepancy arises is when a comparison is made of these results with those obtained by Lewis and von Elbe (1935 *b*) when they substituted almost identical "spectroscopic" molecular heats in some experiments by various investigators. Although these latter experiments were carried out at a comparatively low initial pressure—usually about 1 atm.—they found that, *taking the experiments as a whole*, there was practically no margin for heat loss, the heat capacity of the mixture balancing the heat of reaction. This is not regarded as evidence that there was no heat loss in these explosions but rather as indicating a somewhat high explosion temperature.

The results of the present investigation, so far as the molecular heats of hydrogen and water vapour are concerned, are given in fig. 16. Equations for the curves through the points are given in § 5. For comparison, curves have been added to represent the "spectroscopic" values of Table I, and it will be observed that the present experimental results are about $2\frac{1}{2}$ % above the spectroscopic in the case of water vapour and about 3 % in the case of hydrogen.

4. HEAT LOSS DURING THE PRESSURE-RISE PERIOD

In "matching" the explosions of § 3 (*c*), so as to obtain equality in the percentage of heat loss during the pressure-rise period, an endeavour was made to fulfil three conditions, namely, equality of explosion time, equality of maximum temperature and equality in the proportion of heat lost during a period of 0·1 sec. following the attainment of the maximum pressure. Of these conditions, the third calls for some justification, since it implies that the ratio of the heat loss from the burnt gases under high temperature conditions to the loss which occurs during the spread of flame in the unburnt mixture is constant for all of the mixtures composing a series of "matched" explosions.

A comparison of columns 8 and 12 of Table VI suggests that this assumption is roughly borne out by the results, but this is not very convincing evidence, as the figures of column 12 represent the difference between two large quantities—the heat of reaction and the heat capacity of the gas mixture—and are, therefore, ill-adapted to reflect small variations.

An analysis of the losses before the attainment of the maximum pressure seems to offer a more satisfactory line of attack and, for such an analysis, it is necessary to have data as to the growth of pressure in the explosion vessel as the flame advances from the ignition point to the walls. The requisite information can be obtained by postulating a simple case, and in the calculations underlying the curves of fig. 19 it was assumed (i) that the working fluid is an ideal gas having molecular heats at constant pressure and constant volume of 7·0 and 5·0 respectively; (ii) that during combustion there is no dissociation and no variation in the properties of the gas or in the number of molecules; (iii) that the explosion vessel is a sphere and that its walls are impervious to heat; (iv) that ignition is central and that the flame travels from the centre radially so as to maintain a front concentric with the vessel walls; and (v) that the initial temperature of the charge is 373° C (abs.) and the ratio of the maximum to the initial pressures 23 to 3. On these simple assumptions the rise of pressure is proportional to the mass of charge burnt, and by considering (i) that in the combustion of each elementary mass the temperature rise in that elementary mass is due to constant pressure combustion, (ii) that volume changes in that elementary mass are due to its own large temperature rise and the small pressure rise of the whole mass, (iii) that changes in temperature and volume of the burnt elementary masses are due to adiabatic compression produced by the combustion of subsequent elementary masses, the position of the flame front can be computed from a summation of the volumes of the elementary masses situated between the flame front and the centre of the vessel.

As to the unburnt portion of the gaseous mixture, its temperature is determined from the pressure assuming adiabatic compression. The most striking features of the resulting curves, given in fig. 19, are, first, the long distance the flame must travel at the start of the combustion of the charge to produce an appreciable rise in pressure and, secondly, the large rise of pressure produced by a short travel of the flame at the end of the combustion of the charge. Thus the same rise of pressure is produced by the first 20 % of the flame travel and the last 0·0107 %. It is noteworthy that a pressure curve of very similar shape can be plotted from the figures obtained by Lewis and von Elbe (1934 *a*) from their much more comprehensive calculations in connexion with the spread of flame in an ozone-oxygen explosion.

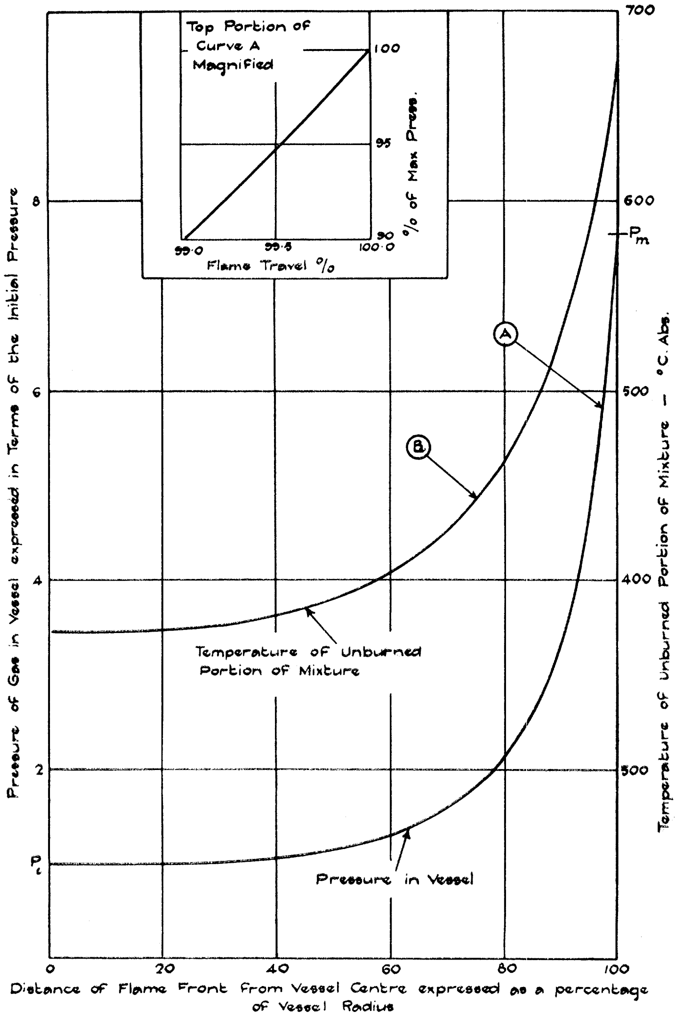

FIG. 19. Hypothetical pressure and temperature diagrams of a "closed vessel" explosion of an ideal gas.

The hypothetical curves of fig. 19 can be used in the study of the heat losses which occur in an actual explosion prior to the maximum pressure. In such an explosion there seem to be three sources of loss, namely, (i) the loss which arises from the compression of unburnt mixture against the walls of the vessel; (ii) the loss due to radiation from the burning gases and the high-temperature burnt gas, and (iii) the loss arising from the contact of the flame, or portions of the flame, with the vessel walls.

The order of magnitude of the loss from the unburnt mixture can be found from a consideration of the difference in temperature between the unburnt layer of gas in contact with the wall and the wall itself. From curve B of fig. 19, it will be seen that although the final adiabatic compression temperature of this layer might reach a figure of about 670° C (abs.), the average temperature *on a flame travel base* is about 423° C (abs.), the corresponding temperature differences between gas and wall being 297 and 50° C. To obtain an average on a time base a record (280) for mixture S 56*d* (Table II and fig. 18) was examined, and here it was found that the maximum adiabatic compression temperature was 606° C (abs.) and the mean 436° C (abs.), the corresponding temperature differences between gas and wall being 233 and 63° C respectively, and the latter 0·27 of the former. In this particular experiment the heat loss in 0·1 sec. after P_m was 7·8 % and the average difference between gas and wall during that period rather over 1900° C. With a difference of 63° C the loss should not exceed $7{\cdot}8 \times \frac{63}{1900}$ or 0·26 %. This is probably a considerable overestimate, but even if it were not so, the loss is of a comparatively small order of magnitude and a 50 % error would not be serious. It may therefore be concluded that, so far as this particular loss is concerned, no serious error would be involved in basing it on the heat-loss measurements made after the maximum pressure.

Considering next the radiation loss during the pressure-rise period, there are grounds for the belief that, with the polished surface used in the experiments, this loss also is small. The evidence is not unquestionable as it involves measurements on the pressure-time record of the progress of the cooling for a couple of seconds or more after the maximum pressure. During a period of this length there may be time for heat to pass through the mica disk covering the manometer diaphragm and cause distortion of the latter. In the initial stages of the cooling this should not occur, and here it is found that the rate of heat loss may be proportional to as much as the eighth power or more of the temperature difference between gas and wall, taking the gas temperature as being that determined from the pressure. The rate of cooling diminishes rapidly, however, and in about half a second it may reach a rate which is roughly proportional to the gas-wall temperature difference and, if the pressure record can be relied upon, this proportionality continues. This suggests that the high rates of cooling closely following the attainment of the maximum pressure are due to the contact of high temperature gases with the vessel wall and that the subsequent establishment of an insulating layer of gas both reduces the rate of loss and makes it conform to conduction proportions. Further, the constant proportionality of the rate of heat loss to the gas-wall temperature difference from about 2000° C (abs.) downwards suggests that radiation is insignificant. On the other hand, the pressure reached in an explosion with a given mixture does not appear to be very sensitive to the condition of the polished surface, an appreciable coating of dust having no effect. This may mean either that the potential loss by radiation is small or that the polished surface is not very effective in reflecting the radiation, and hence a reduction in its efficiency is not readily seen.

If the radiation loss is of negligible dimensions, the third source of loss, that arising from the contact of the flame front with the vessel wall, must be the predominating factor. In the construction of curve A of fig. 19, the flame front is assumed to remain concentric with the vessel wall throughout, and its advance is marked by an increasing rate of pressure rise owing to the increasing area of the flame front itself and the increasing density of the charge that is being burnt. If the flame velocity, relative to the vessel, were constant, then curve A would be a pressure-time record of the process, but it is probable (Lewis and von Elbe 1934 *a*) that the flame velocity first increases and then diminishes to a value less than it had in the initial stages of its travel. The final portion of curve A is so steep, however, that even a 50 % reduction in flame velocity would still mean a very rapid pressure rise. If, in this hypothetical case, the final stages of the combustion make such an effective contribution to the growth of pressure, the question arises as to why, in all but rapid explosions where it is difficult to detect, the explosion record shows a rate of pressure rise which falls off towards the maximum pressure and eventually results in a gradual approach to the latter as will be seen in the photographic reproduction of part of record 280 relating to mixture S 56*d* and given in fig. 18.

The answer seems to be, first, that the flame front is not a smooth surface concentric with the vessel wall and the departure from an increasing rate of pressure rise indicates the point at which portions of the flame front come into contact with the wall; and, secondly, that the final gradual approach to the maximum, which is associated with a comparatively small pressure rise and hence an extremely thin layer of mixture, may be due to the retardation of the combustion of the layer arising from its intimate contact with the relatively cool wall of the explosion vessel. The thickness of the layer must be small, for if it were only four ten-thousandths of the diameter of the vessel—and spread uniformly over the surface—it would contain enough unburnt mixture to give a pressure rise of about 1 % of the whole.

It appears, therefore, from a study of the normal explosion record in conjunction with a hypothetical case, that portions of the flame may be in partial contact with the explosion vessel wall and others in very close proximity to it for an appreciable time before the maximum pressure is reached. During this period the rate of heat loss would be expected to be fairly rapid, and, since the conditions in the explosion vessel just before and just after the maximum pressure must be similar, it would be quite consistent to measure this source of loss before P_m in terms of the loss after P_m.

To sum up, this analysis indicates that, of the three sources of loss into which the total heat loss before P_m may be divided, two appear to be of a small order of magnitude, whereas the third, which is likely to be the cause of the greater part of the loss, is of such a nature as to be measurable on the basis of the heat loss after P_m. Hence the assumption that, with a polished vessel, the rate of heat loss after P_m can be taken as a measure of the heat loss before P_m seems to be reasonable.

5. Summary of results

The values obtained for the mean molecular heats of carbon monoxide, nitrogen, carbon dioxide, hydrogen and water vapour are represented by the appropriate curves given in figs. 13 and 16. The equations of these curves are:

Between 373° C (*abs.*) *and temperatures ranging from* 2370 *to* 3060° C (*abs.*).

$$\begin{aligned}
C_{\mathrm{CO}} &= 4{\cdot}854+0{\cdot}0_{3}7725\,T-0{\cdot}0_{7}875\,T^{2},\\
C_{\mathrm{N_2}} &= 4{\cdot}795+0{\cdot}0_{3}7675\,T-0{\cdot}0_{7}875\,T^{2},\\
C_{\mathrm{CO_2}} &= 8{\cdot}631+0{\cdot}001522\,T-0{\cdot}0_{6}15\,T^{2}.
\end{aligned}$$

Between 373° C (*abs.*) *and temperatures ranging from* 2090 *to* 2930° C (*abs.*).

$$\begin{aligned}
C_{\mathrm{H_2}} &= 4{\cdot}089+0{\cdot}0_{3}953\,T-0{\cdot}0_{7}98\,T^{2},\\
C_{\mathrm{H_2O}} &= 4{\cdot}874+0{\cdot}002284\,T-0{\cdot}0_{6}256\,T^{2},
\end{aligned}$$

where $T=$ upper temperature in ° C abs.

A comparison of these curves, representing the present experimental results, with those drawn through molecular heat values (Table I) obtained by other investigators from spectroscopic data, shows that there is fairly close agreement between the results obtained by these entirely dissimilar methods. The spectroscopist would no doubt interpret these explosion results as a vindication of the accuracy of his own figures, and in view of the precision required in the explosion experiments and the dependency of the results on equilibrium data it would be unwise to quarrel with this conclusion. The present explosion results indicate, however, that the spectroscopic values may be slightly low in the case of carbon dioxide, water vapour and hydrogen, and it must be left to the spectroscopist to determine whether finality has been reached in regard to these gases.

The equations representing the spectroscopic molecular heats of Table I over the temperature ranges already specified are

$$\begin{aligned}
C_{\mathrm{CO}} &= 4{\cdot}955+0{\cdot}0_{3}7018\,T-0{\cdot}0_{7}812\,T^{2},\\
C_{\mathrm{N_2}} &= 4{\cdot}833+0{\cdot}0_{3}7224\,T-0{\cdot}0_{7}822\,T^{2},\\
C_{\mathrm{CO_2}} &= 8{\cdot}672+0{\cdot}001555\,T-0{\cdot}0_{6}18\,T^{2},\\
C_{\mathrm{H_2}} &= 4{\cdot}369+0{\cdot}0_{3}6474\,T-0{\cdot}0_{7}486\,T^{2},\\
C_{\mathrm{H_2O}} &= 5{\cdot}244+0{\cdot}001893\,T-0{\cdot}0_{6}194\,T^{2}.
\end{aligned}$$

6. Acknowledgements

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for the help and data gathered from their publications. Conspicuous amongst the latter are Tizard and Pye's (1923–4) contribution to the Report of the Empire Motor Fuels' Committee and the comprehensive summary of data given by Lewis and von Elbe (1935 *a*).

Appendix I

1. *Method of calculating the composition* of the gaseous mixture at the maximum temperature*

Take, as an example, the nitrogen diluted mixture of the third series of "Matched Explosions", in which the initial temperature was 373·25° C (abs.), the initial pressure 3·722 atm., the maximum explosion pressure 25·07 atm.; the ratio of the "*pv*" of the mixture under the initial pressure and temperature conditions to its ideal value 1·00164; and the initial composition of the mixture in gram-molecules:

$$49{\cdot}852\ \mathrm{CO}+14{\cdot}008\ \mathrm{O_2}+0{\cdot}431\ \mathrm{H_2}+35{\cdot}231\ \mathrm{N_2}+0{\cdot}051\ \mathrm{CO_2}+0{\cdot}427\ \mathrm{Ar}.$$

At the temperature T_e (assumed uniform) and pressure reached in the explosion, the composition of this mixture becomes

$$A.\mathrm{CO_2}+B.\mathrm{CO}+C.\mathrm{H_2O}+D.\mathrm{H_2}+D'.\mathrm{H}+D''.\mathrm{OH}$$
$$+E.\mathrm{O_2}+E'.\mathrm{O}+F.\mathrm{NO}+G.\mathrm{N_2}+G'.\mathrm{N}+0{\cdot}427\,\mathrm{Ar},$$

and the following equations have to be satisfied:

$$\left.\begin{aligned}A+B &= 49{\cdot}903\\ 2A+B+C+D''+2E+E'+F &= 77{\cdot}970\end{aligned}\right\}\text{ and hence } A+C+D''+2E+E'+F = 28{\cdot}067,$$

$$2C+2D+D'+D'' = 0{\cdot}862,$$

$$F+2G+G' = 70{\cdot}462.$$

$$\frac{B.C}{A.D} = K_1,\text{ where }\log K_1 = 1{\cdot}2065-\frac{1100}{T_e},$$

$$\frac{F^2}{G.E} = K_2,\text{ where }\log K_2 = 1{\cdot}348-\frac{9475}{T_e},$$

$$\frac{E.D^2}{C^2} = a.K_3,\text{ where }\log K_3 = 6{\cdot}18-\frac{26400}{T_e},$$

$$\frac{(D')^2}{D} = a.K_4,\text{ where }\log K_4 = 6{\cdot}37-\frac{23820}{T_e},$$

$$\frac{D.(D'')^2}{C^2} = a.K_5,\text{ where }\log K_5 = 7{\cdot}56-\frac{28670}{T_e},$$

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* The use of a calculating machine enabled computations to be made to more figures than can be justified from considerations of the precision of the experimental observations or the formulae employed. An abbreviation of the number of figures shown would, however, have eliminated traces of products which are of interest as traces although they make no appreciable contribution to the magnitude of the relevant results.

$$\frac{(E')^2}{E} = a\,.\,K_6, \text{ where } \log K_6 = 7{\cdot}021 - \frac{26640}{T_e},$$

$$\frac{(G')^2}{G} = a\,.\,K_7, \text{ where } \log K_7 = 7{\cdot}08 - \frac{37920}{T_e},$$

and, as a check, $$\frac{E\,.\,B^2}{A^2} = a\,.\,K_8, \text{ where } \log K_8 = 8{\cdot}593 - \frac{28600}{T_e}.$$

$a = \dfrac{100 \times 373{\cdot}25 \times 1{\cdot}00164}{3{\cdot}722 \times T_e}$ and is introduced to comply with the requirement that the partial pressures of the various gases must be expressed in atmospheres.

Assume $T_e = 2907°$ C (abs.), then:

$$\frac{B\,.\,C}{A\,.\,D} = 6{\cdot}7313;\ \frac{F^2}{G\,.\,E} = 0{\cdot}01226;\ \frac{E\,.\,D^2}{C^2} = 0{\cdot}004335;\ \frac{(D')^2}{D} = 0{\cdot}05182;$$

$$\frac{D\,.\,(D'')^2}{C^2} = 0{\cdot}01722;\ \frac{(E')^2}{E} = 0{\cdot}02485;\ \frac{(G')^2}{G} = 0{\cdot}0_5375 \text{ and } \frac{E\,.\,B^2}{A^2} = 0{\cdot}196422.$$

Assume that $A = 26{\cdot}6663$, then $B = 23{\cdot}2367$ and $\dfrac{D}{C} = 0{\cdot}12945$.

Assume that $C = 0{\cdot}2775$, then $D = 0{\cdot}0359$; $D' = 0{\cdot}0431$ and $D'' = 0{\cdot}1921$ and $2C + 2D + D' + D'' = 0{\cdot}862$ as required.

$$E = 0{\cdot}004336\left(\frac{1}{0{\cdot}12945}\right)^2 = 0{\cdot}2587;\ E' = 0{\cdot}0802.$$

Assume $G = 35{\cdot}0586$, then $F = 0{\cdot}3334_5$ and $G' = 0{\cdot}0115$ and $F + 2G + G' = 70{\cdot}462$ as required.

Finally, $A = 28{\cdot}067 - C - D'' - 2E - E' - F = 26{\cdot}6663$, which is in agreement with the value assumed.

The composition of the gas mixture at $T_e = 2907°$ C (abs.) is:

$CO_2 = 26{\cdot}6663$
$CO = 23{\cdot}2367$
$H_2O = 0{\cdot}2775$
$H_2 = 0{\cdot}0359$
$H = 0{\cdot}0431$
$OH = 0{\cdot}1921$
$O_2 = 0{\cdot}2587$
$O = 0{\cdot}0802$
$NO = 0{\cdot}3335$
$N = 0{\cdot}0115$
$N_2 = 35{\cdot}0586$
$Ar = 0{\cdot}4270$
Total mols. $= 86{\cdot}6211$

The assumed value of T_e must now be checked against the value obtained from the experimental observations and the computed molecular concentration. On the latter basis

$$T_e = 373{\cdot}25 \times \frac{25{\cdot}07}{3{\cdot}722} \times \frac{100}{86{\cdot}621} \times 1{\cdot}00164$$
$$= 2907° \text{ C (abs.)},$$

which is in agreement with the value assumed.

It will be realized that the values assumed for T_e, A and C may be the result of many previous trials, although only the final calculations are given here.

2. *Method of determining the temperature-gradient correction*

The example taken is the determination of the temperature-gradient correction for the mixture given in the preceding section. The first step is the simplification of the mixture in order to shorten the calculations.

(*a*) *The mixture.* The simplification of the mixture, so as to limit its constituents to the three main gases CO, O_2 and N_2, and still retain the same explosion temperature and pressure, involves a reduction in the proportion of O_2 in order to compensate for such factors as the elimination of heat loss and the use of spectroscopic heat capacities (Table I). This reduction leads to a diminution—as compared with the experimental mixture—in the concentration of uncombined O_2, atomic oxygen and nitric oxide in the gas mixture at the explosion temperature and, with a view to counteracting this, some modification was made in the ratio of CO to N_2. The result is essentially a compromise, the simplified mixture having the composition

$$48{\cdot}85\ CO + 13{\cdot}448\ O_2 + 37{\cdot}702\ N_2,$$

which at a temperature of 2907° C (abs.) becomes, on basis of formulae given in the preceding section:

$$25{\cdot}9704\ CO_2 + 22{\cdot}8796\ CO + 0{\cdot}2527\ O_2 + 0{\cdot}0792\ O \\ + 0{\cdot}341\ NO + 0{\cdot}0119\ N + 37{\cdot}5256\ N_2,$$

the total mol. being 87·0604 and the maximum pressure 25·23 atm. To bring this pressure of 25·23 atm. into line with the experimental value of 25·07 atm., the initial pressure was reduced to 3·69 atm. for association with an initial temperature of 373·13° C (abs.).

(*b*) *The history of elementary masses.* The mixture composition and its initial and explosion pressures having been settled, the next step is the determination of the history of elementary masses from which the distribution of (i) temperature, (ii) internal energy, and (iii) the product of temperature and molecular concentration, throughout the whole mass can be inferred.

Consider an elementary mass situated on the edge of the zone of combustion when 0·6 of the whole mass has already been burnt.

Assuming the rise of pressure is proportional to the mass of charge burnt, its pressure will already have been raised from 3·69 atm. to $\{3{\cdot}69 + 0{\cdot}6\ (25{\cdot}07 - 3{\cdot}69)\} = 16{\cdot}518$ atm., and on the basis of the compression being adiabatic, the heat capacities being those of Table I and R having a value of 1·9869, the resulting rise in temperature will be found to be from 373·13 to 567·06° C (abs.).

The elementary mass is then burnt at the constant pressure of 16·518 atm. and its rise of temperature found by equating the heat released by the chemical reactions to that expended in raising the gas temperature. As the rise of temperature is independent of the mass of mixture, it is convenient to consider 100 mol. The mixture

$$48{\cdot}85\ CO+13{\cdot}448\ O_2+37{\cdot}702\ N_2$$

becomes after combustion

$$A\,.\,CO_2+B\,.\,CO+E\,.\,O_2+E'\,.\,O+F\,.\,NO+G'\,.\,N+G\,.\,N_2,$$

where, for any *guessed* temperature, the values of A, B, etc. can be determined on the lines indicated in the preceding section of this Appendix, taking

$$a=\frac{A+B+E+E'+F+G'+G}{16{\cdot}518}.$$

In this case a guessed temperature—after combustion—of 2653·5° C (abs.) gave a composition* at this temperature and 16·518 atm. of

$$26{\cdot}6756\ CO_2+22{\cdot}1744\ CO+0{\cdot}0495\ O_2+0{\cdot}0158\ O$$
$$+0{\cdot}1056\ NO+0{\cdot}0035\ N+37{\cdot}6475\ N_2,$$

the total number of gram-molecules being 86·6719.

From the molecular heats of Table I, the mean heat capacity of this mixture at constant volume per degree temperature rise between 373·13 and 567° C (abs.) is 530·465 cal., and between 373·13 and 2653·5° C (abs.), 679·479 cal., giving a value of 693·33 cal. between 567 and 2653·5° C (abs.). The addition of 86·6719 × 1·9869, i.e. 172·208 cal., converts these quantities to constant pressure conditions and hence the heat capacity per degree at constant pressure between 567 and 2653·5° C (abs.) is 865·538 cal.

The heat generated by combustion at constant pressure is

$$26{\cdot}6756\times 67825{\cdot}2-0{\cdot}1056\times 21550-0{\cdot}0158\times 59450-0{\cdot}0035\times 84835=1{,}805{,}766,$$

in accordance with the computed values of heats of combustion at constant pressure in relation to initial temperature. Hence rise of temperature on combustion

$$=\frac{1{,}805{,}766}{865{\cdot}538}=2086{\cdot}29^\circ\ C,$$

and temperature at end of combustion $=567{\cdot}06+2086{\cdot}29^\circ\ C=2653{\cdot}35^\circ\ C$ (abs.). This is in agreement with the temperature guessed. Therefore at the end of the constant pressure combustion stage the elementary mass has a temperature of 2653·3° C (abs.).

The final stage in the history of the elementary mass under consideration is its adiabatic compression from 16·518 to 25·07 atm. and the resulting temperature has to be determined. As the result is independent of the mass, the equivalent of 100 mol. of the unburnt mixture will be taken. Curves of the type shown in fig. 10 are constructed

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* See footnote on the first page of this Appendix (p. 203).

from which the internal energy (heat plus chemical) and the molecular concentration of the burnt mixture at any relevant temperature can be read, the pressure being 25·07 atm. and the internal energy being measured above 373·13° C (abs.). A final temperature of 2836° C (abs.) is guessed, and from the curves just mentioned the internal energy is found to be 1,733,300 cal. and the molecular concentration 86·877.

Prior to compression the internal energy was 1,567,714 cal., the heat energy portion being $679{\cdot}479 \times 2280{\cdot}22 = 1{,}549{,}362$ cal. and the chemical energy portion, estimated from the conversion of

$$\left.\begin{array}{lr} O_2 \text{ to } CO_2 \text{ being} & 2\times 0{\cdot}0495\times\ \ 67{,}390 = 6672 \\ O \text{ to } CO_2 \text{ being} & 0{\cdot}0158\times 126{,}220 = 1994 \\ N \text{ to } N_2 \text{ being} & 0{\cdot}0035\times\ \ 84{,}185 = \ \ 295 \\ NO \text{ to } CO_2 \text{ and } N_2 \text{ being} & 0{\cdot}1056\times\ \ 88{,}930 = 9391 \end{array}\right\} = 18{,}352 \text{ cal.},$$

whereas the molecular concentration was 86·6719. Hence on the basis of the guessed final temperature, the change in internal energy is $(1{,}733{,}300-1{,}567{,}714)=165{,}586$ for a change of temperature of $(2836-2653{\cdot}35) = 182{\cdot}65°$ C and the mean molecular concentration is $\frac{1}{2}(86{\cdot}877+86{\cdot}6719) = 86{\cdot}7745$. Therefore the mean *apparent* molecular heat, at constant volume, over this temperature range is

$$\frac{165{,}586}{86{\cdot}7745\times 182{\cdot}65} = 10{\cdot}4475,$$

and at constant pressure this becomes $10{\cdot}4475+1{\cdot}9869 = 12{\cdot}4344$,

$$\frac{\gamma-1}{\gamma} = 1-\frac{10{\cdot}4475}{12{\cdot}4344} = 0{\cdot}1598,$$

and the final temperature $= 2653{\cdot}35\times\left(\dfrac{25{\cdot}07}{16{\cdot}518}\right)^{0{\cdot}1598} = 2836{\cdot}29°$ C (abs.), which is in practical agreement with the temperature guessed. Therefore the temperature of the elementary mass after its final compression is 2836·29° C (abs.) and the internal energy (above 373·13° C (abs.)) associated with it is found from the internal energy curve to be 1,733,500 cal. reduced in the ratio of this elementary mass to 100 g.-mol.

The value of the product of temperature and mol. is $2836{\cdot}29\times 86{\cdot}8776 = 246{,}410$ reduced in like fashion.

(*c*) *The temperature gradient, etc.* By plotting the data obtained from a number of suitably situated* elementary masses, the distribution of temperature, internal energy and the temperature × mol. product in relation to the whole mass can be shown.

Since the explosion pressure is a function of temperature and molecular concentration, the integration of the temperature × mol. curve enables the associated explosion

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* Elementary masses were taken at the beginning and end of the combustion, and on the edge of zones representing the combustion of 0·2, 0·4, 0·6, 0·8, and in some cases 0·1, of the whole mass.

pressure to be computed. The value obtained by graphical integration is 252,955 and hence the explosion pressure $= 3{\cdot}69 \times \dfrac{252{,}955}{373{\cdot}13 \times 100} = 25{\cdot}015$ atm.

Consider this to be the explosion pressure given in an actual experiment and determine the *conventional* explosion temperature by the method given in § 1 of this Appendix. *Its value will be found to be* 2905·6° C (*abs.*). Therefore from an explosion pressure of 25·015 atm. the conventional method of computing the explosion temperature would have given 2805·6° C (abs.).

To find the temperature when the gradient is smoothed out without heat loss, integrate the internal energy curve. The value thus obtained for the total internal energy is 1,824,000 cal. By the use of the method of § 1 of this Appendix and the heat capacities of Table I, the temperature is found at which the burnt gases contain this internal energy. *This was found to be* 2916·68° C (*abs.*). Therefore, when the temperature is equalized, its value becomes 2916·68° C (abs.) and the pressure rises to

$$3{\cdot}69 \times \frac{2916{\cdot}68}{373{\cdot}13} \times \frac{87{\cdot}0912}{100} = 25{\cdot}1205 \text{ atm.}$$

From this it is concluded:

(i) that the *conventional* explosion temperature—based on the explosion pressure—is 2905·6° C (abs.),

(ii) the required uniform temperature is 2916·68° C (abs.),

(iii) the gradient correction is 11·08° C.

It will be observed that although the calculations of temperature distribution, etc. were based on an assumed and desired explosion pressure of 25·07 atm., the explosion pressure obtained was somewhat less than this, namely, 25·015 atm. Small discrepancies between the assumed and computed explosion pressures were generally found, but they were regarded as being too small to warrant any revision of the calculations.

In applying the gradient correction to the actual explosion mixture, the calculated adjustment can be made to either its explosion pressure or explosion temperature. The result would be the same if the variation in the molecular concentration with change in temperature were identical in the experimental mixture and its simplified version. In the fourth series of the "Matched Explosions", where the departure from this condition was the most, the gradient correction was applied to the explosion pressure, whereas in the other three series it was applied to the explosion temperature.

3. *Method of determining the molecular heat of a gas in terms of that of argon*

Take, for example, the mixtures S 67*a* and S 70*c* of Table IV and obtain the mean molecular heat of nitrogen in terms of the heat capacity of argon. From the composition of the mixtures (see Table IV) at the gradient corrected maximum temperatures, the quantities of heat released by the chemical reactions up to this point can be determined.

The quantities are 1,308,410 and 1,787,734 cal./100 mol. of original mixture for S 67*a* and S 70*c* respectively, the latter being made up as follows:

From the formation of	CO_2	$(26{\cdot}5996-0{\cdot}0510=26{\cdot}5486)\times 67{,}390=$	1,789,110
” ”	H_2O	$0{\cdot}2738\ \times 57{,}660=$	15,787
” ”	H	$-0{\cdot}0444\ \times 51{,}610=$	−2,291
” ”	OH	$-0{\cdot}1990\ \times\ 5{,}890=$	−1,172
” ”	O	$-0{\cdot}0866\ \times 58{,}830=$	−5,095
” ”	NO	$-0{\cdot}3510\ \times 21{,}540=$	−7,561
” ”	N	$-0{\cdot}0124\ \times 84{,}185=$	−1,044
			1,787,734

Most of this heat, represented by the fractions P and P', is stored in the respective high-temperature gas mixtures and would be given out by them in cooling, without chemical change, to the initial temperature of about 373° C (abs.). Hence:

For S 67*a*:

$$\begin{aligned}&19{\cdot}2468\,C_{CO_2}+17{\cdot}4542\,C_{CO}+0{\cdot}4572\,C_{H_2O}+0{\cdot}0611\,C_{H_2}+0{\cdot}0526\,C_{H}\\&\quad+0{\cdot}2309\,C_{OH}+0{\cdot}2159\,C_{O_2}+0{\cdot}0692\,C_{O}+0{\cdot}0321\,C_{NO}+0{\cdot}0011\,C_{N}\\&\quad+0{\cdot}3634\,C_{N_2}+52{\cdot}0700\,C_{Ar}=\frac{1{,}308{,}410\times P}{2933{\cdot}2-373{\cdot}5}\\&\quad=511{\cdot}159\,P.\end{aligned}$$

For S 70*c*:

$$\begin{aligned}&26{\cdot}5996\,C_{CO_2}+23{\cdot}3034\,C_{CO}+0{\cdot}2738\,C_{H_2O}+0{\cdot}0355\,C_{H_2}+0{\cdot}0444\,C_{H}\\&\quad+0{\cdot}1990\,C_{OH}+0{\cdot}2785\,C_{O_2}+0{\cdot}0866\,C_{O}+0{\cdot}3510\,C_{NO}+0{\cdot}0124\,C_{N}\\&\quad+35{\cdot}0493\,C_{N_2}+0{\cdot}4270\,C_{Ar}=\frac{1{,}787{,}734\times P'}{2918{\cdot}2-373{\cdot}2}\\&\quad=702{\cdot}450\,P'\\&\text{or when corrected}=701{\cdot}526\,P\ \text{(see below).}\end{aligned}$$

Multiplying S 67*a* by 701·526/511·159 and subtracting the result from S 70*c* gives

$$\begin{aligned}&0{\cdot}1841\,C_{CO_2}-0{\cdot}6511\,C_{CO}-0{\cdot}3537\,C_{H_2O}-0{\cdot}0484\,C_{H_2}-0{\cdot}1179\,C_{OH}\\&\quad-0{\cdot}0178\,C_{O_2}+0{\cdot}3069\,C_{NO}+34{\cdot}5506\,C_{N_2}-0{\cdot}0253\,C_{\text{mono.}}=71{\cdot}0350\,C_{Ar}.\end{aligned}$$

Expressing all the quantities on the left-hand side in terms of C_{N_2} by the use of the ratios of C_{CO_2}, C_{CO}, C_{H_2O}, and C_{H_2} to C_{N_2} already obtained from previous analyses of the experimental results as a whole, and by the use of the ratios of C_{OH}, C_{O_2} and C_{NO} to C_{N_2} as given by the "spectroscopic" values of Table I, the equation reduces to

$$33{\cdot}8492\,C_{N_2}=71{\cdot}0603\,C_{Ar},$$

the heat capacity of the monatomic gases H, O and N being added to the right-hand side of the equation. From the above

$$\boldsymbol{C_{N_2} = 2{\cdot}0993\ C_{Ar}}$$

(or if $C_{Ar} = 2{\cdot}98$, then $C_{N_2} = 6{\cdot}256$), the temperature range being 373–2933° C (abs.).

The correction applied to S 70*c* during the above solution was to compensate for the failure of the nitrogen experiments to fulfil the exact "matching" conditions. The explosion times of S 70*c* and S 67*a* were the same and hence no adjustment was required on this account, but the rates of heat loss during these times—as determined from the mean rates of heat loss during the 0·1 sec. immediately following the maximum pressure—differed considerably, as will be seen from Table VI and were in the ratio 12·38 to 10·94. To apply a correction for this discrepancy it is necessary to known the order of the heat loss prior to T_m in the case of the argon explosion S 67*a*. From previous analyses of the experimental results, it is possible to express C_{CO_2}, C_{CO}, C_{N_2}, C_{H_2O} and C_{H_2} in terms of C_{Ar} employing values read off curves through the experimental points, and Table I enables the molecular heats of the remaining gases of the high temperature mixture of S 67*a* to be expressed in a similar manner. The heat capacity equation of S 67*a* therefore reduces to

$$169{\cdot}095\, C_{Ar} = 511{\cdot}159\, P,$$

taking $C_{Ar} = 2{\cdot}98$, then $P = 0{\cdot}9858$ and heat loss $= 0{\cdot}0142$ of the reaction heat. The corresponding heat loss of S 70*c* is $0{\cdot}0142 \times 12{\cdot}38/10{\cdot}94 = 0{\cdot}0161$ and $P' = 0{\cdot}9839$, and thus $(0{\cdot}9839/0{\cdot}9858)\, P$ can be substituted for P' in S 70*c*.

There is one further correction to be applied and that is for the difference in the explosion temperatures T_m, namely, 15° C. The mean heat capacity per degree of the high temperature mixture of S 67*a* relates to the range 373·5–2933·2° C (abs.), whereas in the corresponding mixture of S 70*c* the range is 373·2–2918·2° C (abs.). The amount by which the figure for the heat capacity per degree in the latter case must be increased to make it apply to the wider temperature range of S 67*a* can be determined from results already obtained from previous analyses or from the "spectroscopic" values of Table I. It amounts to 1 part in 1629.

Taking the original figure for the heat capacity per degree of S 70*c* and applying these corrections,

$$702{\cdot}450\ P' \text{ becomes } 702{\cdot}450 \times \frac{0{\cdot}9839\ P}{0{\cdot}9858} \times \frac{1630}{1629} = \boldsymbol{701{\cdot}526\ P}$$

as taken above.

APPENDIX II

Specific volume of superheated steam at 100° C

In the explosion experiments on mixtures containing water vapour, it was necessary to know the specific volume of steam at 100° C and at pressures below atmospheric.

There was no apparatus available for making measurements of such quantities, and consequently a thorough search of the literature was made. It was found that specific volumes had been measured for a very wide range of pressures above atmospheric and at temperatures from 100 to about 500° C, but, with the exception of the work of Maass and Mennie, to which reference will be made later, there appeared to be no experimental data for the required pressure range. It was finally decided to employ one of the pressure-volume-temperature formulae which have been published from time to time to cover the range of superheated steam employed in practice.

During the last decade or so there has been great activity in Europe and America in connexion with the compilation of the International Steam Tables ("Progress in Steam Research", 1926, 1929, 1932, 1933; Osborne and others 1930; Keyes and Smith 1931; Smith and Keyes 1931; Knoblauch and others 1932; Keyes and others 1934; Steam Tables 1935; Osborne and others 1935, 1937; Keyes and others 1935, 1936; Havliček and Miskovsky 1936; Koch 1937; Schmidt 1938). In 1934, Keyes, Smith and Gerry of the Massachusetts Institute of Technology devised a formula connecting pressure, volume and temperature, and compared values computed by the formula with the experimental results of Knoblauch, Linde and Klebe (1905) and with their own practical values. In the former case there was quite substantial agreement between the two sets of figures, the overall deviation being 0·149 %, whilst even better agreement was obtained in the latter comparison. The same authors published a modified form of their equation in 1935 and derived heat capacities, enthalpy and Joule-Thomson values from it which were found to be in good agreement with the measurements made elsewhere in America (Osborne and others 1930, 1935). The formula is reproduced later in this Appendix together with the constants computed by the present authors for 100° C. These calculations gave a value of specific volume at atmospheric pressure of 1673·1 c.c./g., which compares favourably with the figure of 1673·2 c.c./g. accepted by the Third International Steam Tables Conference (1935), the values of 1673·1, 1673·3 and 1673·5 c.c./g. put forward at various times by the Bureau of Standards (Keyes and Smith 1931; Osborne and others 1935, 1937), the figure of 1672·2 c.c./g. deduced by Havliček and Miskovsky (1936) from a formula said to represent the best line through their experimental results, and the value of 1673·0 c.c./g. deduced by the present authors from a formula devised by Koch (1937) and Schmidt (1938) in connection with the preparation of the V.D.I. steam tables.

Specific volume values for the required pressure range were given in the steam tables published in 1932 by Knoblauch, Raisch, Hausen and Koch. A comparison was made of the values obtained from these tables and those computed by means of the Massachusetts Institute of Technology formula, and when a large scale plotting was made of pressure × volume against pressure, it was found that the two sets of values agreed well at pressures up to 350 mm. abs., but began to depart above this pressure until at 760 mm. the Massachusetts Institute of Technology formula value was approximately 1 part in 880 lower than that from the tables. The specific volume values of the tables were given for simple fractions of 1 kg./sq. cm. and thus no value was given for 1 atm., the nearest figure being for 1 kg./sq. cm. The specific volume value for 1 atm. was obtained from the curve through the tables' values of pressure × volume and was 1675·7 c.c./g., which does not agree with the values given in the preceding paragraph.

Maass and Mennie (1926) published values of the pressure due to various masses of water enclosed in a measured volume and heated to various temperatures. It was found possible to plot their results and interpolate values to 100° C. The values obtained in this way covered the range 316–700 mm. and, when plotted upon the diagram mentioned above, they were found to be in substantial agreement with the curve obtained by use of the Massachusetts Institute of Technology formula, particularly in view of the fact that Maass and Mennie's claim to accuracy was not greater than 1 in 1000 to 1 in 2000.

From this survey of the literature, it appears permissible to assume that the Massachusetts Institute of Technology formula will give substantially reliable values at pressures below atmospheric. The formula, when computed for 100° C, is as follows:

$$V = RT/P + B,$$

where

$V =$ specific volume of steam in c.c./g.,
$R =$ gas constant $= 4\cdot55504$,
$P =$ pressure in international atmospheres,
$T = 273\cdot16 + t^\circ$ C,

$$B = B_{01} + B_{01}^2\, g_1(\tau)\,\tau P + B_{01}^4\, g_2(\tau)\,\tau^3 P^3 - B_{01}^{13}\, g_3(\tau)\,\tau^{12} P^{12},$$

where

$\tau = 1/T$,
$B_{01} = 1\cdot89 - 2641\cdot62 \times 10^{80870.\tau^2}$,
$g_1(\tau) = 82\cdot546\tau - 1\cdot6246 \times 10^5\tau^2$,
$g_2(\tau) = 0\cdot21828 - 1\cdot2697 \times 10^5\tau^2$,
$g_3(\tau) = 3\cdot635 \times 10^{-4} - 6\cdot768 \times 10^{64}\tau^{24}$.

At 100° C:

$t = 100$ and hence $T = 373\cdot16$ and $RT = 1699\cdot7587$,
$B_{01} = -25\cdot071$,
$g_1(\tau) = -0\cdot945484$ and $B_{01}^2\, g_1(\tau)\,\tau = -1\cdot592584$,
$g_2(\tau) = -0\cdot693544$ and $B_{01}^4\, g_2(\tau)\,\tau^3 = -0\cdot00527321$,
$g_3(\tau) = -1273\cdot4381$ and $B_{10}^{13} g_3(\tau)\,\tau^{12} = 0\cdot0_9 270064$,

whence

$$\boldsymbol{V = \frac{1699\cdot7587}{P} - 25\cdot071 - 1\cdot592584\, P - 0\cdot00527321\, P^3 - 0\cdot0_9 270064\, P^{12}}.$$

The last term is obviously negligible for pressures of 1 atm. or less, and, in such cases, it is also possible to omit many of the integers in the other terms.

SUPPLEMENT

THE EXPERIMENTAL DETERMINATION OF THE COMPRESSIBILITY OF GASES

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1. Introduction

During the course of an experimental redetermination of the specific heat of gases at high temperatures that was carried out at the N.P.L. for the D.S.I.R., the need arose for data on the compressibility of gas mixtures over moderate ranges of pressure and at temperatures of 20 and 100° C. Various theoretical solutions were considered, and finally it was decided to construct the necessary apparatus and make the determinations experimentally.

Although the data obtained have been used in connexion with the main investigation, it seems to be worth while to put on record a description of the apparatus used and the technique employed in the hope that other investigators may be able to take advantage of the writers' experience and so save valuable time in the earlier stages of their work.

The method employed for determining the pressure and volume changes was that in which a vessel of known volume is charged with the gas or gas mixture to the required upper pressure and its contents expanded to atmospheric pressure and their volume measured. It has been used by several investigators, not only recently (Scott 1929), but as far back as the middle of the last century (Natterer 1850–5).

2. Apparatus

(*a*) *Description*. Although the principle is the same, the apparatus used by various investigators has differed in detail. The apparatus employed by the writers was based on that developed in the High Pressure Gas Laboratories of the Imperial College of Science and Technology, as described in a paper (Scott 1929) on the compressibility of hydrogen and carbon monoxide and mixtures of those gases. The method of calibrating the high-pressure vessel was also gleaned from the same paper. Considerable modifications have, however, been introduced which make for ease of manipulation and, it is considered, a higher degree of precision. These comprise: (i) the use of compensating tubes for automatically eliminating the effects of changes in atmospheric pressure and water-bath temperature that may occur during the volume measuring process; (ii) the use of a special water bath to ensure good circulation and uniformity of temperature; (iii) the use of special devices for the fine adjustment of mercury levels in the measuring vessels; and (iv) the use of an oil U-tube for pressure-balancing purposes.

A diagrammatic sketch of the apparatus is shown in fig. 20. It consists of a steel pressure vessel F of about 100 ml. capacity and three glass measuring tubes E, D and C having capacities of approximately 100, 50 and 60 ml., the last-named being subdivided into millilitres and tenths. The stems of the measuring vessels are made of capillary tubing carrying fine lines to indicate the volume limits of the vessels. The upper stems are connected by three-way glass taps to a horizontal length of glass capillary tubing which carries an oil U-tube and a mercury U-tube at one end and can be coupled to the steel pressure vessel at the other. The lower stems of the vessels are coupled by rubber pressure tubing to the two pipe-lines leading to the mercury reservoirs. Screw clips on the rubber connexions are specially provided for the fine adjustment of the mercury levels in the tubes when the glass taps have been closed. The steel pressure vessel also has a stem of small capacity and a screw-down valve—the small stem capacity being obtained by inserting in the stem bore a solid steel rod of somewhat smaller diameter.

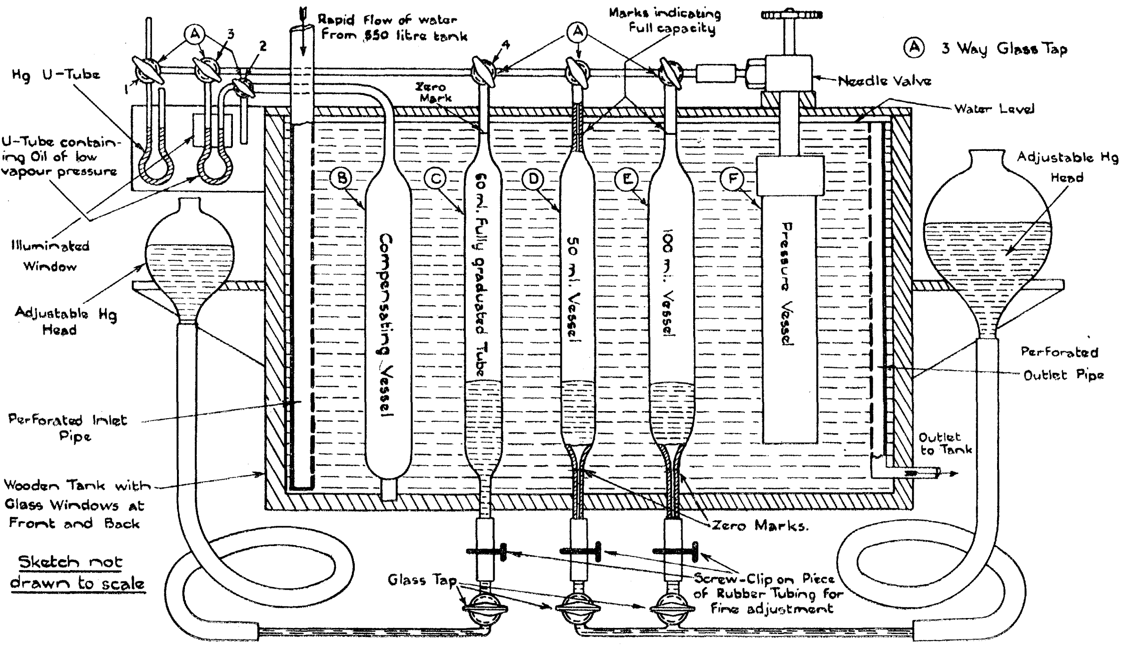

FIG. 20. Sketch of compressibility apparatus.

The glass compensating vessel B has a capacity of about 100 ml. and is coupled, at first by capillary tubing and then by larger tubing, to the free limb of the oil U-tube—a three-way tap (2) being provided to permit connexion with the atmosphere. The three-way tap (1) is for a similar purpose, whereas that marked (3) is required for shutting off the oil U-tube whilst the measuring vessels are being charged with gas, the mercury U-tube being used for maintaining the pressure more or less atmospheric during this filling process.

The water for the bath is pumped from, and returns to, a lagged tank of about 120 gal. (550 l.) capacity. The water enters by *two* perforated pipes fitted at one end of the bath and leaves by two similar pipes at the other. The outlet pipes are fitted with perforated sleeves whose position can be adjusted so as to alter the size of the apertures through which the water flows. Adjustments can then be made so as to ensure that some water will flow over the open upper ends of the tubes and thus maintain the water level. The bath temperature is read by means of a "calorimeter" thermometer, graduated to 0·01° C. It was found necessary to fit a gauze filter on the inlet to the bath to prevent the perforations becoming choked and this filter was made so that it could be readily removed and cleaned.

(*b*) *Calibration.* The glass vessels were calibrated by weighing their mercury content. In the case of the two vessels *D* and *E* whose limits were defined by fine lines on their capillary inlet and outlet tubes, high degrees of accuracy were readily obtainable, the measurements in millilitres being 50·1835, 50·1825, 50·1829 and 50·1827 in the case of the smaller vessel and 99·4227, 99·4211 and 99·4211 in the case of the larger. The calibrations of the graduated tube at intervals of 1 ml. could not be repeated with the same precision, for although a reading microscope was employed the thickness of the graduation lines and the comparatively large bore of the tube, etc. mitigated against extreme accuracy. Two calibrations were made and agreed to within about 0·01 ml. on the average, the maximum deviation being nearly 0·03 ml. in one case. Although the deviations tend to be smoothed out by the curve that is drawn through the readings, they still indicate the limit of accuracy that may be expected from readings in the fully graduated tube.

The volume of the steel pressure vessel could not be determined by a mercury filling, but the method used by Scott seemed to be applicable. This method was tried and a considerable time was spent in making refinements to it—such as the addition of a compensating vessel—and in developing the necessary technique. When this had been accomplished, the method proved to be exceedingly sensitive and gave results which could be measured to a single drop of mercury weighing about 0·063 g. and having a volume of about 0·005 ml. The three final calibrations gave values of 94·8618, 94·8587 and 94·8634 ml. at 20° C. A diagram of the final form of the calibration apparatus is shown in fig. 21.

The calibration is effected by the transfer of air from the glass vessel *A* to the previously evacuated pressure vessel *F*, the volume of air transferred being determined from the quantity of mercury required to replace it. The passage of air into the pressure vessel and its replacement by mercury take place slowly and simultaneously, so that the air pressure in vessel *A* remains more or less constant as shown by the oil U-tube.

In applying the method it was soon evident that fluctuations in atmospheric pressure during an experiment would have to be eliminated and that the water-bath would have to be made as efficient as possible. It was therefore decided to couple to the atmospheric limb of the oil U-tube a compensating vessel *B*, in which the atmospheric pressure at the commencement of the experiment would be retained and by which the effects of any variations in bath temperature would be eliminated. Arrangements were also made for circulating water through the bath as in the case of the apparatus illustrated in fig. 20.

The delivery of the exact quantity of mercury into vessel *A* required a considerable amount of care and skill and was aided by the provision of a fine capillary jet of the type shown and also by the fitting of a short length of rubber pressure tubing between the jet and the mercury reservoir. The rubber tubing was fitted with two screw-down pipe clips so that the upper one could be closed when the requisite quantity of mercury had nearly been delivered and the lower one subsequently manipulated so as to squeeze from the rubber tube the additional quantity of mercury needed to effect a balance. The initial and final balances were made with the mercury set at the top of the glass

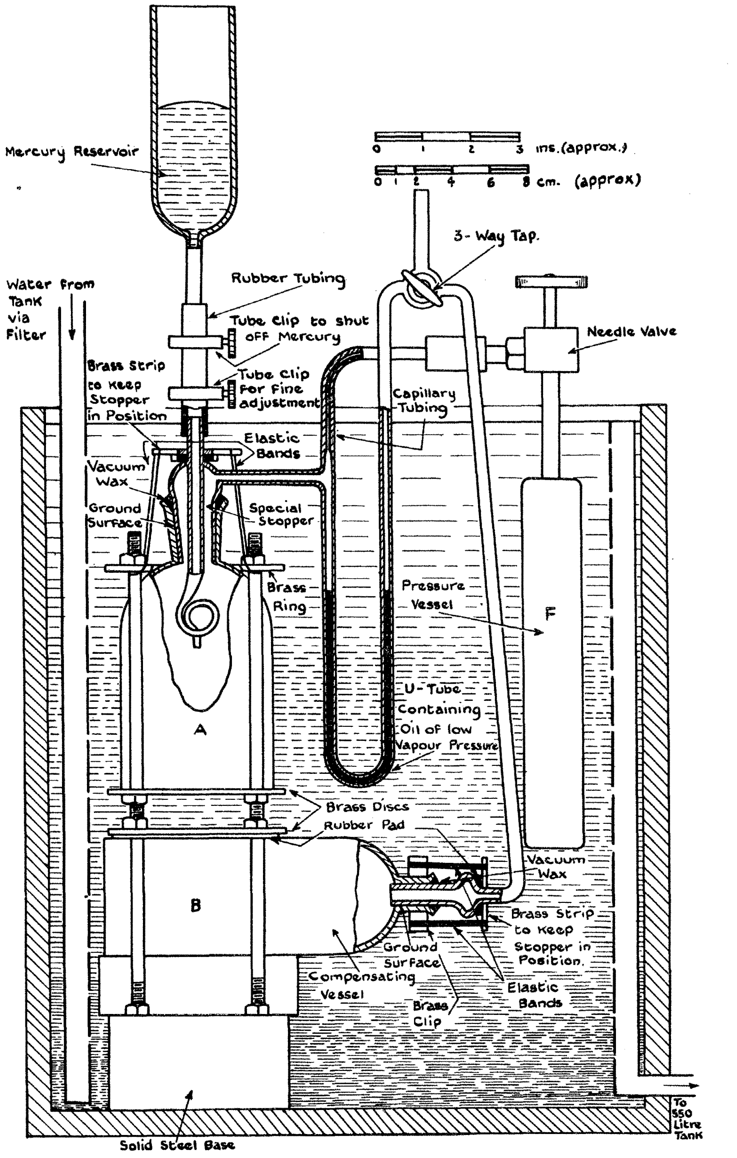

FIG. 21. Sketch of apparatus for the determination of volume of pressure vessel.

spiral. On unscrewing the lower clip the mercury in the jet was drawn back so that it was safe to remove the apparatus from the bath and dry and dismantle it for the purpose of weighing the mercury in vessel A.

It should be mentioned that the oil level in the U-tube was set in relation to the cross-hair in a reading microscope and proved very responsive to small pressure changes.

There is one important factor to refer to before concluding this description of the calibration of the pressure vessel, and that is the necessity for using comparatively dry air in vessel A. The use of atmospheric air gave unreliable results, due possibly to the deposition of moisture in the stem of the pressure vessel during the early stage of the expansion of the air and the apparent failure of this moisture to re-evaporate.

Air from a high-pressure air bottle was blown into A before the stopper was finally inserted in position, and hence the water vapour content should be very small.

(*c*) *Experimental procedure.* The experimental procedure is naturally dependent on the degree of accuracy required, and the present notes are intended to relate to high precision work.

The glass measuring vessels and oil U-tube of fig. 20 are prepared for the measurement of a volume of gas or gas mixture by their preliminary exposure for some 12 hr. or so to the gas or gas mixture concerned. These vessels and the left-hand limb of the U-tube are charged several times and then left full of the gas or gas mixture. This precaution is taken, first, to saturate as far as possible the oil in the U-tube and, secondly, to put the inside surfaces of the glass vessels in such a condition that they are unlikely to give off any water vapour.

The steel pressure vessel is placed in a well-stirred water-bath of very large capacity and charged with gas or gas mixture to the pressure and temperature required, the latter being fixed by the bath temperature. The pressure should be measured by a sensitive device such as a temperature-controlled mercury column for the lower pressures or say a loaded piston pressure gauge for the higher pressures (Glazebrook 1922).

The pressure vessel is then coupled up to the system of measuring vessels shown in fig. 20, precautions having been taken to see that its valve is properly closed and that the packing round the valve spindle is making a sufficiently gas-tight joint.

The glass measuring vessels are then charged with mercury to their full capacity marks, whilst the water in the bath is being circulated and is getting into a steady temperature condition, the temperature of the large mass of water in the main tank having already been adjusted to that required, say 20° C.

When the bath temperature has become steady, a few more minutes are allowed to elapse during which the cross-hair in a reading microscope is accurately set at the height of the oil meniscus in one limb of the U-tube. During this time the three-way taps marked (1) and (2) have been continuously or intermittently open to the atmosphere, and when everything is ready the bath temperature is read and arrangements are made for the reading of a high-precision barometer and the simultaneous closing of the taps

(1) and (2) to atmosphere. The barometer reading gives the pressure of the air in the compensating vessel *B*.

Before letting any gas out of the pressure vessel and into the measuring system the tap (3) is turned so as to isolate the attached limb of the U-tube temporarily and so prevent the oil being blown out should the pressure in the measuring system accidentally rise sufficiently to do so. A *slight* suction is also put on the system by a lowering of the mercury level in the stem of vessel *C*.

The needle valve on the pressure vessel is then opened very slightly and about 10 ml. admitted to vessel *C* before the complete filling of vessels *D* and *E*. During the filling process the mercury reservoirs are lowered by hand so as to maintain the pressure in the measuring system as nearly atmospheric as possible as indicated by the mercury U-tube. When the filling of vessels *D* and *E* is complete, the needle valve on the pressure vessel and the lower taps on the measuring vessels are closed and the mercury level in tubes *D* and *E* is accurately adjusted by the screw clips. The level of the mercury in vessel *C* is then adjusted so as to balance the pressure of the gas in the measuring vessel, first, against that of the atmosphere by means of the mercury U-tube and, finally, against the pressure in the compensating vessel *B*.

Before discharging the contents of vessels *D* and *E*, the three-way tap is closed to vessel *C* so as to retain this unmeasured portion of gas, and the oil U-tube is isolated by closing tap (3).

Having discharged the gaseous contents of vessels *D* and *E*, the filling of both or one of them is continued as before until a residual quantity is reached which can be measured in the graduated tube *C*. A microscope fitted with a small aperture is used for reading the level of the mercury meniscus in tube *C*, and the necessary band of light behind the meniscus is provided by fitting a slotted blind to the back of the water-bath and illuminating the slot by a powerful but somewhat distant lamp. An illuminated window is also provided behind the oil U-tube.

A summation of the volumes measured gives the final volume required at the atmospheric pressure and the bath temperature pertaining when the compensating vessel was isolated from the atmosphere at the commencement of the measuring process. This volume will have to be corrected if any variations in the capacity of the connecting tubes, etc. have occurred. For example, in opening the needle valve, a small portion of valve spindle is withdrawn from the tube system, and hence the volume of the latter has been increased by this amount and the corresponding correction must be added to the measured volume of the expanded gas.

The volume of this tube system should be kept as small as possible, for although it is supposed to contain a constant mass of gas that supposition will not be realized if the atmospheric pressure varies during an experiment or if the temperature of the tube system alters. The error due to variation in atmospheric pressure can be eliminated by making the technique more elaborate, and a system of jacketing has in fact been applied to the tube system for the purpose of keeping its temperature constant. The latter is not shown in fig. 20, but consists of a system of small lead tubes, which can be bound to the glass tube, and through which some of the bath circulating water is caused to pass.

3. Examples of results obtained at 20° C

The first experiments made with this apparatus were carried out on hydrogen, and they serve to check the results given by the apparatus as a whole against those obtained by other investigators.

As accurate measurements of pressures by means of a mercury column were limited to about 5 atm., Schalkwijk's (1901) results were considered to be the most appropriate with which to make a comparison, for they extended to comparatively low pressures of the order of 7 atm. and appear to have been carried out with great care.

Several experiments were, therefore, made in which the pressure vessel was charged with hydrogen to about 5 atm. and the volume of its contents measured at atmospheric pressure, and from the results obtained the volume of the pressure vessel was deduced using Schalkwijk's* formula for the compressibility of hydrogen. The figures obtained in this way for the volume of the pressure vessel were: 94·8560, 94·8935, 94·8681 and 94·8568 ml., giving a mean of 94·8686 ml. This compares favourably with the figure obtained by direct calibration, viz. 94·8613 ml., and hence the apparatus as a whole seemed to be satisfactory. About a year later the volume of the pressure vessel was again determined from similar hydrogen experiments, although in this case two of the charging pressures were rather less than 4 atm. The values obtained were: 94·8585, 94·8845, 94·8775, 94·8185 and 94·8542, and if those relating to the lower charging pressure are given half-weight, the weighted mean becomes $94{\cdot}862_3$ ml., which is still nearer to the measured value.

The apparatus was used for measuring the compressibility of a variety of mixtures both at 20 and at 100° C. Examples of the results are given in fig. 22, but the tests in general related to mixtures of such diverse compositions that the results could not be illustrated by curves of this type. The accuracy is probably of the order of 1 part in 2000.

4. Compressibility characteristics at 100° C

The apparatus—with a small addition—has also been used for determining the departure from the perfect gas state of a large number of gas mixtures when their temperature is 100° C and their pressure P a few atmospheres, not exceeding 5.

Each determination requires a couple of experiments and in addition it is necessary

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* Schalkwijk's equation for hydrogen at 20° C is

$$pv = 1{\cdot}07258 + 0{\cdot}6351 \times 10^{-3}p + 0{\cdot}206 \times 10^{-6}p^2,$$

where p is in international atmospheres and v is the volume occupied by the gas at 1 atm. at 0° C.

to know the coefficient of cubical expansion, α, of the pressure vessel itself, a quantity which was deduced from linear expansion measurements.

In the first experiment the pressure vessel is charged with the gas mixture to a pressure of about $P \times \frac{293}{373}$ at 20° C and the volume of its contents determined at atmospheric pressure and the same temperature, namely, 20° C. From the two *pv* products thus obtained, the corresponding value of *pv* under infinitely low pressure conditions is computed by assuming a linear relationship between *pv* and $1/v$, and extrapolating to $1/v = 0$. In order to convert these *pv* products from 20 to 100° C, the *pv* value applying to infinitely low density is multiplied by 373/293, whereas the other *pv* product relating to 20° C and the upper pressure must be multiplied by the ratio of the *pressures* at 100 and 20° C when the density remains constant. The estimation of this pressure ratio is the reason for the second experiment.

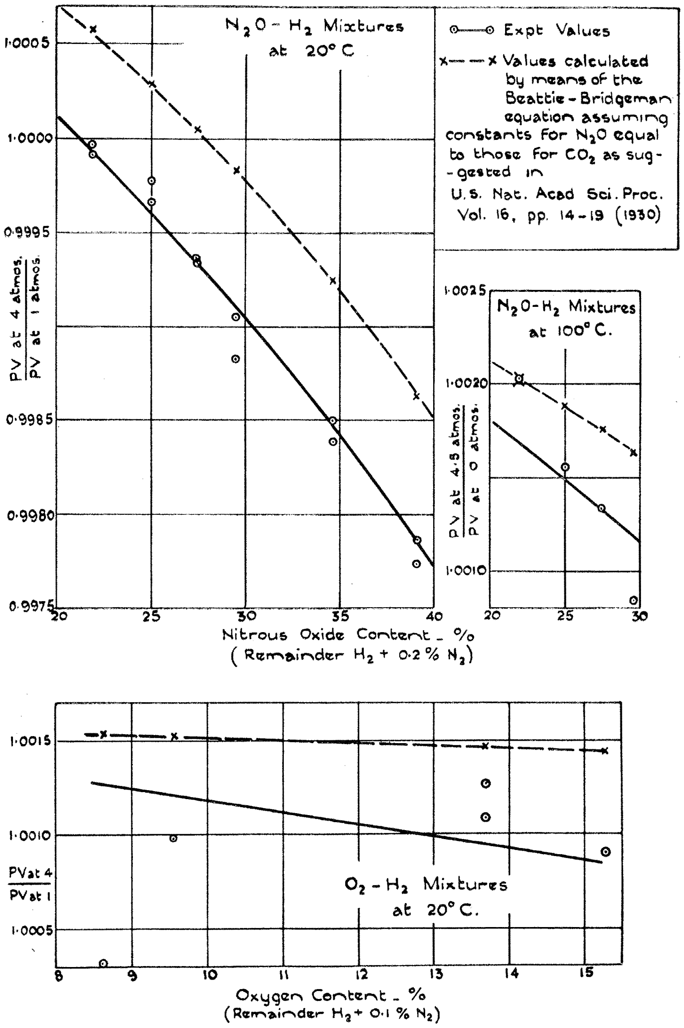

FIG. 22. Gas mixtures. Comparison of compressibility values computed from experimental data with those calculated by the Beattie-Bridgeman equation of state.

In this experiment the pressure vessel is placed in a steam-bath, specially constructed on the hypsometer principle, and charged with the gas mixture to the pressure *P*. After cooling from 100 to 20° C, the contents of the pressure vessel are expanded to atmospheric pressure and their volume determined at 20° C. This volume is then reduced to compensate for the expansion of the pressure vessel between 20 and 100° C and compared with the expanded gas volume given by the first experiment at 1 atm. and 20° C. From this comparison the pressure reached on cooling at constant volume from 100° C and *P* to 20° C can be closely estimated, and hence the required pressure ratio determined.* It will, of course, be realized that where atmospheric pressure is mentioned in connexion with this pair of experiments a constant value is implied.

The method was "tried out" on hydrogen and the following values of the ratio of the pv at 100° C and about 4·9 atm. to the ideal pv were obtained: $1{\cdot}0033_4$, $1{\cdot}0032_3$ and $1{\cdot}0036_4$. According to the Beattie-Bridgeman equation (1928) this ratio should be 1·00234.

5. EXPERIMENTAL OBSERVATIONS RELATING TO THE APPARATUS AND TECHNIQUE

In the experiments to which allusion has already been made no consistent steps were taken to dry the glass surfaces of the measuring vessels. Occasionally the vessels were subjected to a fairly high vacuum for this purpose, but usually they were left full of atmospheric air between the various experiments and put into use after merely displacing that air by mercury.

The agreement between the hydrogen results given by the apparatus and those obtained by other investigators seemed to show that the drying of vessels, that had merely been exposed to unsaturated atmospheric air, was unnecessary.

When most of the experimental work had been done, however, some experiments appeared to show that errors of the order of 1 part in 1000 to 1 part in 3000 might arise if precautions were not taken to dry the vessels; and although the experimental evidence was obscured by other creep effects for which it is difficult to account, it seems well worth while to take the precaution of exposing the measuring vessels for a considerable time to the type of gas which they will be required to measure. An instruction to this effect has been included in § 2 (*c*).

To test the effect of taking this precaution, two further experiments were made on hydrogen. In these experiments the measuring vessels were exposed to the "dry" gas for a considerable time before use, and in addition the tube system used for coupling up the measuring vessels, U-tubes, etc. was partially jacketed in an endeavour to keep its temperature constant.

The values of the volume of the pressure vessel deduced from these experiments, on the basis of Schalkwijk's compressibility formula, were found to be 94·8707 and 94·8541 ml. The mean of these, namely, 94·860 is almost the same as the weighted

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* A typical calculation is given in the Appendix to this supplement.

mean of the previous set of determinations, namely, 94·862; and it differs by about 1 part in 10,000 from the mean (94·869) obtained in the first set of experiments.

Although this appears to show that the "water-vapour effect" is negligibly small, other experiments indicate that it is not quite safe to draw this conclusion, and hence it is recommended that the suggested precaution of exposing the vessels to the gas to be measured should be observed.

The reference to some experiments that indicated slight creep effects requires some amplification. It was found that when a fresh charge of "dry" hydrogen was put into vessel D after the latter had been exposed to the same type of gas for 12 hr. or more, the volume did not remain quite constant but expanded very slowly—the increase being, in one case, about 0·015 ml. in 45 min. It is, of course, of a very small order, and it serves to illustrate the sensitivity of the apparatus, but on the other hand it calls for some explanation. The possibility of there being a *very small* infiltration of water into vessel D was examined by subjecting that vessel to internal gas pressure and searching for any sign of a leak. No leak was discovered by this means, and subsequently a further examination was made by putting the vessel under a vacuum and exploring its surface by means of a Tesla High-Frequency Vacuum Tester, with the same negative result. The phenomenon probably has a very simple explanation, but time was not available for pursuing the matter further.

6. CONCLUSION

The apparatus described appears to be capable of giving results with a high degree of precision, provided a very accurate and sensitive instrument for measuring the atmospheric pressure is installed in the immediate vicinity and accurate means are available for measuring the upper pressure.

7. ACKNOWLEDGEMENTS

The authors desire to put on record their indebtedness to the Barometer Section of the Metrology Department of the N.P.L., and especially to Mr F. D. Jones, for the high-precision barometer readings that were so essential a factor in this investigation.

APPENDIX TO SUPPLEMENT

Method of experiment and calculation to get the ratio

$$\frac{pv \text{ at } 4{\cdot}5 \text{ atm. (abs.)}}{pv \text{ at } 0 \text{ atm. (abs.)}} \text{ at } 100^\circ \text{ C.}$$

Take the mixture S 82 which consists of $27{\cdot}431\,N_2O + 72{\cdot}409\,H_2 + 0{\cdot}160\,N_2$. The charge pressure of 4·5 atm. at 100° C is equivalent to a charge pressure at 20° C of $4{\cdot}5 \times 293/373 = 3{\cdot}535$ atm., which was the pressure aimed at in Exp. I.

Exp. I. Pressure vessel charged at 20° C

Charge pressure.

Volume of pressure vessel at 20° C = 94·861 ml.

Mercury U-tube readings = 5812·8 mm.
3895·2

Difference = 1917·6 mm.

Temperature of U-tube case = 19·2° C.

Applying corrections to the U-tube reading for the expansions of the mercury and the steel scale, vernier and scale calibrations, and for the differences in level of the various parts of the apparatus, the U-tube reading becomes

= 1912·06 mm.

Corrected barometer reading at time of charge = 766·62

Thus charge pressure = 2678·68 mm.

Temperature of pressure vessel water-bath at time of charge = 20·023° C
= 293·153° C abs.

$$\text{Charge pressure at } 293{\cdot}130^\circ \text{ C abs.} = \frac{2678{\cdot}68 \times 293{\cdot}130}{760{\cdot}00 \times 293{\cdot}153} = 3{\cdot}524303 \text{ atm. (abs.)}$$

Expansion pressure.

Expansion pressure is equivalent to the barometer reading at
the instant of closing taps 1 and 2 = 766·67 mm.

Temperature of bath containing glass measuring vessels at
this time was = 19·995° C
= 293·125° C abs.

$$\text{Expansion pressure at } 293{\cdot}130^\circ \text{ C abs.} = \frac{766{\cdot}67 \times 293{\cdot}130}{760{\cdot}00 \times 293{\cdot}125} = 1{\cdot}0087936 \text{ atm. (abs.)}$$

Volume of contents of pressure vessel when expanded.

1 filling of tube E = 99·422 ml.

2 fillings of tube D = 100·366

Reading of 37·00 ml. on tube C = 36·923

Allowance for withdrawal of pressure vessel valve spindle = 0·014

Volume of gas remaining in pressure vessel = 94·861

Total volume of gas = 331·586 ml.

Exp. II. Pressure vessel charged at 100° C

Reading of water U-tube attached to pressure vessel steam-bath = 4·8 cm., which is equivalent to 3·54 mm. of mercury.

Corrected barometer reading at time of charge = 766·80 mm.
Steam pressure = 770·34 mm.
Pressure vessel temperature at time of charge = 100·379° C
= 373·509° C abs.
Coefficient of linear expansion of pressure vessel = $11{\cdot}6 \times 10^{-6}$
Volume of pressure vessel at 100·379° C = 95·1264 ml.

Charge pressure.

Mercury U-tube readings 6189·4 mm.
3520·9
Difference = 2668·5 mm.
Temperature of U-tube case = 21·1° C
When corrected as before, U-tube reading = 2659·66 mm.
Corrected barometer reading at time of charge = 766·80
Thus charge pressure = 3426·46 mm.

Charge pressure at 373·509° C *abs.* = 3426·46/760·00 = 4·50850 atm. (abs.).

Expansion pressure.

Expansion pressure is equivalent to the barometer reading at the instant of closing taps 1 and 2 = 766·80 mm.
Temperature of water-bath containing glass measuring vessels at this time was = 19·992° C
= 293·122° C abs.

$$\text{Expansion pressure at } 293{\cdot}130^\circ\text{ C abs.} = \frac{766{\cdot}80 \times 293{\cdot}130}{760{\cdot}00 \times 293{\cdot}122} = 1{\cdot}008975 \text{ atm. (abs.)}$$

Volume of contents of pressure vessel when expanded.

1 filling of tube *E* = 99·422 ml.
2 fillings of tube *D* = 100·366
Reading of 38·48 ml. on tube *C* = 38·408
Allowance for withdrawal of pressure vessel valve spindle = 0·014
Volume of gas remaining in pressure vessel = 94·861
Total volume of gas = 333·071 ml.

Calculation of results

Exp. I. At 293·130° C abs. a gas volume of 94·861 ml. at a pressure of 3·524303 atm. became a volume of 331·586 ml. when expanded under a pressure of 1·0087936 atm.

$$\text{Thus}\quad \frac{PV \text{ at } P = 3{\cdot}524303 \text{ atm.}}{PV \text{ at } P = 1{\cdot}0087936 \text{ atm.}} = \frac{3{\cdot}524303 \times 94{\cdot}861}{1{\cdot}0087936 \times 331{\cdot}586} = 0{\cdot}9994532. \tag{1}$$

Assume an equation of the form $PV = A + B/V$.

Let $PV = 1$ when $P = 1{\cdot}0087936$ atm., then

$$1 = A + 1{\cdot}0087936B. \tag{2}$$

$PV = 0{\cdot}9994532$ when $P = 3{\cdot}524303$ atm., hence $1/V = 3{\cdot}5262310$ and

$$0{\cdot}9994532 = A + 3{\cdot}5262310B, \tag{3}$$

$$(3) - (2) \quad -0{\cdot}0005468 = 2{\cdot}5174374B.$$

Thus $$B = -0{\cdot}0002172.$$

Substituting in (2) $$A = 1{\cdot}0002191.$$

$$\boldsymbol{PV = 1{\cdot}0002191 - 0{\cdot}0002172/V.} \tag{4}$$

If $P = 1$, $PV = 1{\cdot}0000019$, and

$$\frac{PV \text{ at } P = 3{\cdot}524303 \text{ atm.}}{PV \text{ at } P = 1 \text{ atm.}} = \frac{0{\cdot}9994532}{1{\cdot}0000019} = \mathbf{0{\cdot}9994_5 \text{ at } 20^\circ \text{C}.}$$

This is the method used to obtain the results at 20° C as given in fig. 22.

Exp. II. From (4) PV at $P = 0$ atm. at 293·130° C abs. $= 1{\cdot}0002191$.

Thus PV at $P = 0$ atm. at 373·509° C abs. $= 1{\cdot}0002191 \times 373{\cdot}509/293{\cdot}130$

$$= 1{\cdot}2744886. \tag{5}$$

A gas volume of 95·1264 ml. at 4·50850 atm. at 373·509° C abs. gave a volume of 333·071 ml. at 293·130° C abs. when expanded under a pressure of 1·008975 atm.

If the cylinder volume had been 94·861 ml. at the time of charge instead of 95·1264 ml. and the expansion pressure had been 1·0087936 atm. instead of 1·008975 atm., the expanded volume of the gas would have been

$$\frac{333{\cdot}071 \times 94{\cdot}861 \times 1{\cdot}008975}{95{\cdot}1264 \times 1{\cdot}0087936} = 332{\cdot}201_5 \text{ ml.}$$

In Exp. I an expanded volume of 331·586 ml. was given by a charge pressure of 3·524303 atm.; thus, under similar conditions, a volume of $332{\cdot}201_5$ ml. would be given by a charge pressure at 20° C of

$$\frac{3{\cdot}524303 \times 332{\cdot}2015}{331{\cdot}586} = 3{\cdot}530845 \text{ atm.}$$

(This assumes no change in the PV ratio from 3·524303 to 3·530845 atm.)

From this it follows that a pressure of 3·530845 atm. at 293·130° C abs. is equivalent to 4·50850 atm. at 373·509° C abs., and the ratio of the increase of pressure produced by such a temperature rise = 4·50850/3·530845 = 1·276890.

This pressure ratio × PV value of Exp. I = 0·9994532 × 1·276890 = 1·2761918.

(5) gave PV ratio at P = 0 atm. at 373·509° C abs. = 1·2744886.

$$\textbf{At 373·509° C abs. (100·379° C)}\ \frac{\boldsymbol{PV}\ \textbf{at}\ \boldsymbol{P} = \textbf{4·50850 atm.}}{\boldsymbol{PV}\ \textbf{at}\ \boldsymbol{P} = \textbf{0 atm.}} = \frac{1{\cdot}2761918}{1{\cdot}2744886} = \mathbf{1{\cdot}0013_4}.$$

SUMMARY

In view of the experience gained at the N.P.L. in connexion with investigations involving the explosion of gas mixtures in closed vessels, it was decided that an attempt should be made to redetermine the specific heat of certain gases at high temperatures by the use of the explosion method.

By carrying out explosions of mixtures of the type $(2+a)\,CO+O_2+b.Ar$ and replacing the argon in turn by CO, N_2 and CO_2, values have been obtained of the mean molecular heat of these gases above 373° C (abs.) and over the range 2370–3060° C (abs.). By balancing the heat losses in each group of explosions, the direct measurement of such heat losses was avoided although their magnitude has, as a matter of interest, been deduced subsequently from the heat capacity equations.

Determinations have also been made of the mean molecular heats at constant volume of H_2 and H_2O (gas), the measurements being made from 373° C (abs.) to temperatures ranging from about 2090 to 2930° C (abs.). Although the highest temperature is considerably below that attained in the case of CO, N_2 and CO_2, it is believed to be a considerable advance on earlier work, the temperature extension being obtained by the substitution of nitrous oxide for oxygen in the explosive mixtures. The H_2 and H_2O determinations are dependent on heat loss measurements for which a special device was employed.

The values obtained for the mean molecular heats at constant volume of CO, N_2, CO_2, H_2 and H_2O (gas) are represented by the following equations over the specified temperature ranges:

Between 373° C (*abs.*) *and temperatures ranging from* 2370 *to* 3060° C (*abs.*):

$$\begin{aligned} C_{CO} &= 4{\cdot}854+0{\cdot}0_3 7725\,T-0{\cdot}0_7 875\,T^2, \\ C_{N_2} &= 4{\cdot}795+0{\cdot}0_3 7675\,T-0{\cdot}0_7 875\,T^2, \\ C_{CO_2} &= 8{\cdot}631+0{\cdot}001522\,T-0{\cdot}0_6 15\,T^2. \end{aligned}$$

Between 373° C (*abs.*) *and temperatures ranging from* 2090 *to* 2930° C (*abs.*):

$$\begin{aligned} C_{H_2} &= 4{\cdot}089+0{\cdot}0_3 953\,T-0{\cdot}0_7 98\,T^2, \\ C_{H_2O} &= 4{\cdot}874+0{\cdot}002284\,T-0{\cdot}0_6 256\,T^2, \end{aligned}$$

where T = upper temperature in ° C abs.

These values are compared with molecular heats deduced by other investigators from spectroscopic data and, for the ranges specified above, represented by

$$\begin{aligned}
C_{\mathrm{CO}} &= 4{\cdot}955+0{\cdot}0_{3}7018T-0{\cdot}0_{7}812T^{2},\\
C_{\mathrm{N_2}} &= 4{\cdot}833+0{\cdot}0_{3}7224T-0{\cdot}0_{7}822T^{2},\\
C_{\mathrm{CO_2}} &= 8{\cdot}672+0{\cdot}001555T-0{\cdot}0_{6}18T^{2},\\
C_{\mathrm{H_2}} &= 4{\cdot}369+0{\cdot}0_{3}6474T-0{\cdot}0_{7}486T^{2},\\
C_{\mathrm{H_2O}} &= 5{\cdot}244+0{\cdot}001893T-0{\cdot}0_{6}194T^{2}.
\end{aligned}$$

The difference between the two sets of values—obtained by such diverse methods—is small in the case of CO, N_2 and CO_2 but larger in the case of H_2 and H_2O (gas). The larger discrepancy associated with the last-mentioned gases may be mainly due to the less satisfactory experimental procedure.

Supplement

The information that was required on the compressibility characteristics of gas mixtures at medium pressures, in connexion with the main paper, led to this quantity being obtained experimentally. The supplement gives a description of the apparatus that was used for the purpose and particulars of its calibration. It also gives examples of the departure of certain gas mixtures from the ideal state both at 20 and 100° C. The apparatus is regarded as being suitable for work of high precision provided it is used in conjunction with sufficiently sensitive instruments for measuring temperature and pressure.

REFERENCES

Awbery, J. H. and Griffiths, E. 1933 *Proc. Roy. Soc.* A, **141**, 1–6.
Beattie, J. A. and Bridgeman, O. C. 1928 *J. Amer. Chem. Soc.* **50**, 3133.
Bone, W. A. and Haward, W. A. 1921 *Proc. Roy. Soc.* A, **100**, 67–84.
Briner, E., Boner, J. and Rothen, A. 1926 *J. Chim. Phys.* **23**, 788–807; *Helv. chim. Acta*, **9**, 634–48.
Clayton, J. O. and Giauque, W. F. 1932 *J. Amer. Chem. Soc.* **54**, 2610–26.
David, W. T. and Davies, W. 1930 *Phil. Mag.* **9**, 390–401.
Davis, C. O. and Johnston, H. L. 1934 *J. Amer. Chem. Soc.* **56**, 1045–7.
Fenning, R. W. 1924 *Rep. Memor. Aero. Res. Comm., Lond.*, no. 902.
— 1925 *Rep. Memor. Aero. Res. Comm., Lond.*, no. 979.
— 1926 *Philos. Trans.* A, **225**, 331–56.
Fenning, R. W. and Cotton, F. T. 1933 *Proc. Roy. Soc.* A, **141**, 17–28.
Fenning, R. W. and Tizard, H. T. 1927 *Proc. Roy. Soc.* A, **115**, 318–33.
Giauque, W. F. 1930*a* *J. Amer. Chem. Soc.* **52**, 4808–15.
— 1930*b* *J. Amer. Chem. Soc.* **52**, 4816–31.
Giauque, W. F. and Clayton, J. O. 1933 *J. Amer. Chem. Soc.* **55**, 4875–89.
Giauque, W. F. and Overstreet, R. 1932 *J. Amer. Chem. Soc.* **54**, 1731–44.
Glazebrook, R. 1922 *Dictionary of applied physics*, **1**, 630.
Gordon, A. R. 1934 *J. Chem. Phys.* **2**, 65–72 and 549.
Havliček, J. and Miskovsky, L. 1936 *Helv. phys. Acta*, **9**, 161–207.

Johnston, H. L. and Chapman, A. T. 1933 *J. Amer. Chem. Soc.* **55**, 153–72.

Johnston, H. L. and Davis, C. O. 1934 *J. Amer. Chem. Soc.* **56**, 271–6.

Johnston, H. L. and Dawson, D. H. 1933 *J. Amer. Chem. Soc.* **55**, 2744–53.

Johnston, H. L. and Walker, M. K. 1933*a* *J. Amer. Chem. Soc.* **55**, 172–86.

— — 1933*b* *J. Amer. Chem. Soc.* **55**, 187–93.

— — 1935 *J. Amer. Chem. Soc.* **57**, 682–84.

Kassel, L. S. 1934 *J. Amer. Chem. Soc.* **56**, 1838–42.

Keyes, F. G. and Smith, L. B. 1931 *Mech. Engng, N.Y.*, **53**, 132–5.

Keyes, F. G., Smith, L. B. and Gerry, H. T. 1934 *Mech. Engng, N.Y.*, **56**, 87–92.

— — — 1935 *Mech. Engng, N.Y.*, **57**, 164 and 176.

— — — 1936 *Proc. Amer. Acad. Arts. Sci.* **70**, 319–64.

Knoblauch, O., Linde, R. and Klebe, H. 1905 *Mitt. Forsch. Geb. Ing.*, V.D.I. No. 21.

Knoblauch, O., Raisch, E., Hausen, H. and Koch, W. 1932 *Tabellen und Diagramme für Wasserdampf.*

Koch, W. 1937 *V.D.I.-Wasserdampftafeln mit einem Mollier* (*i.s.*) *Diagram auf einer besonderen Tafel.*

Lewis, B. and von Elbe, G. 1933*a* *J. Amer. Chem. Soc.* **55**, 507–11.

— — 1933*b* *J. Amer. Chem. Soc.* **55**, 511–19.

— — 1934*a* *J. Chem. Phys.* **2**, 283–90.

— — 1934*b* *J. Chem. Phys.* **2**, 291–3.

— — 1934*c* *J. Chem. Phys.* **2**, 665–8.

— — 1934*d* *J. Chem. Phys.* **2**, 659–64.

— — 1935*a* *J. Amer. Chem. Soc.* **57**, 612–14.

— — 1935*b* *J. Chem. Phys.* **3**, 63–71.

Maass, O. and Mennie, J. H. 1926 *Proc. Roy. Soc.* A, **110**, 198–232.

Natterer 1850 *S.B. Akad. Wiss. Wien*, **5**, 351.

— 1851 *S.B. Akad. Wiss. Wien*, **7**, 557.

— 1854 *S.B. Akad. Wiss. Wien*, **12**, 199.

— 1855 *Ann. Phys., Lpz.*, **94**, 436.

Osborne, N. S., Stimson, H. F. and Fiock, E. F. 1930 *Trans. A.S.M.E.* **52**, paper FSP 52–28.

Osborne, N. S., Stimson, H. F. and Ginnings, D. C. 1935 *Mech. Engng, N.Y.*, **57**, 162–3.

— — — 1937 *Bur. Stand. J. Res., Wash.*, **18**, 389–447.

Pier, M. 1909 *Z. Elektrochem.* **15**, 536–40.

"Progress in Steam Research" 1926 *Mech. Engng, N.Y.*, **48**, 151–60.

— 1929 *Mech. Engng, N.Y.*, **51**, 123–9.

— 1932 *Mech. Engng, N.Y.*, **54**, 118–27.

— 1933 *Mech. Engng, N.Y.*, **55**, 113–17.

Rossini, F. D. 1931*a* *Bur. Stand. J. Res., Wash.*, **6**, 1–36.

— 1931*b* *Bur. Stand. J. Res., Wash.*, **6**, 37–50.

— 1931*c* *Bur. Stand. J. Res., Wash.*, **7**, 329–30.

Schalkwijk, J. C. 1901 *Commn. Phys. Lab. Leiden*, no. 70.

Schmidt, E. 1938 *Z. Ver. dtsch. Ing.* **82**, 49–51.

Scott, G. A. 1929 *Proc. Roy. Soc.* A, **125**, 330.

Smith, L. B. and Keyes, F. G. 1931 *Mech. Engng, N.Y.*, **53**, 135–7.

Steam Tables, Report of 3rd Int. Conference 1935 *World Power*, 172–5.

Tizard, H. T. and Pye, D. R. 1923–4 *Rep. Emp. Motor Fuels Comm., I.A.E.* **18**, part I, 33–37 and 46.

Wohl, K. and von Elbe, G. 1929 *Z. phys. Chem.* B, **5**, 241–71.

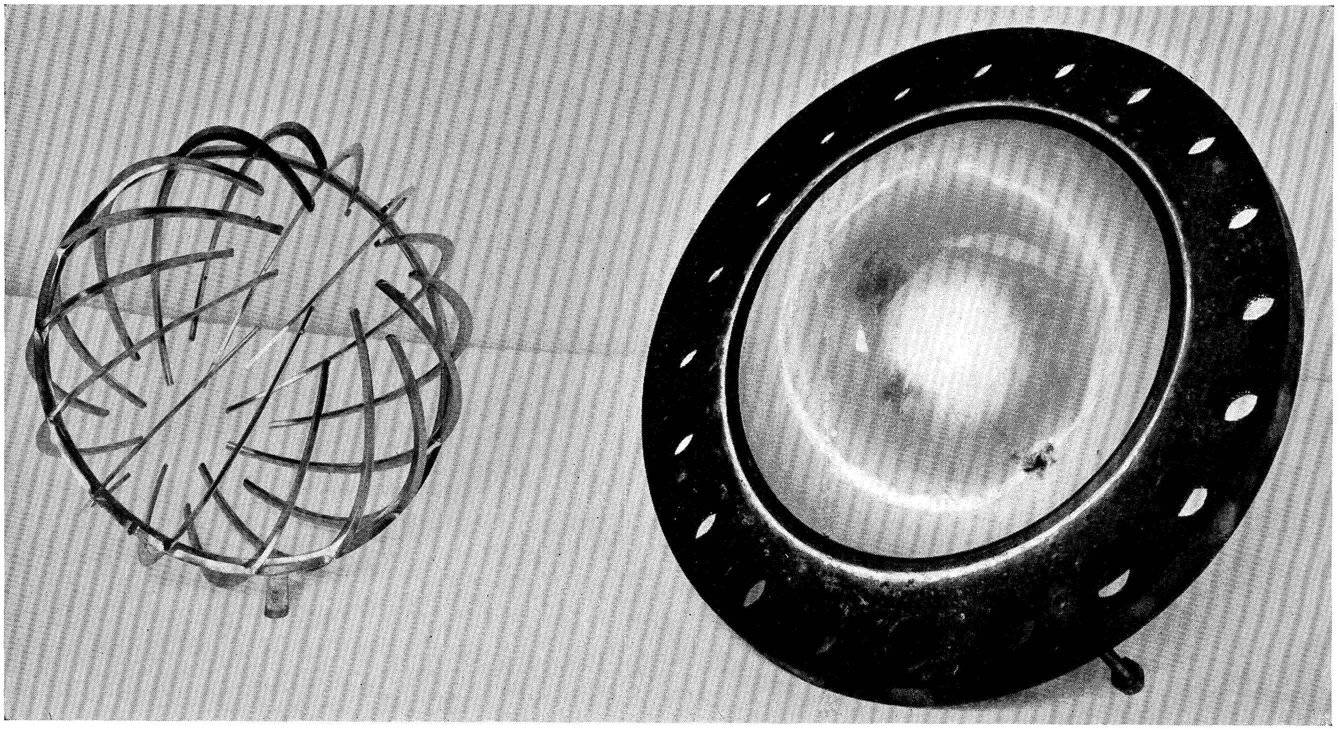
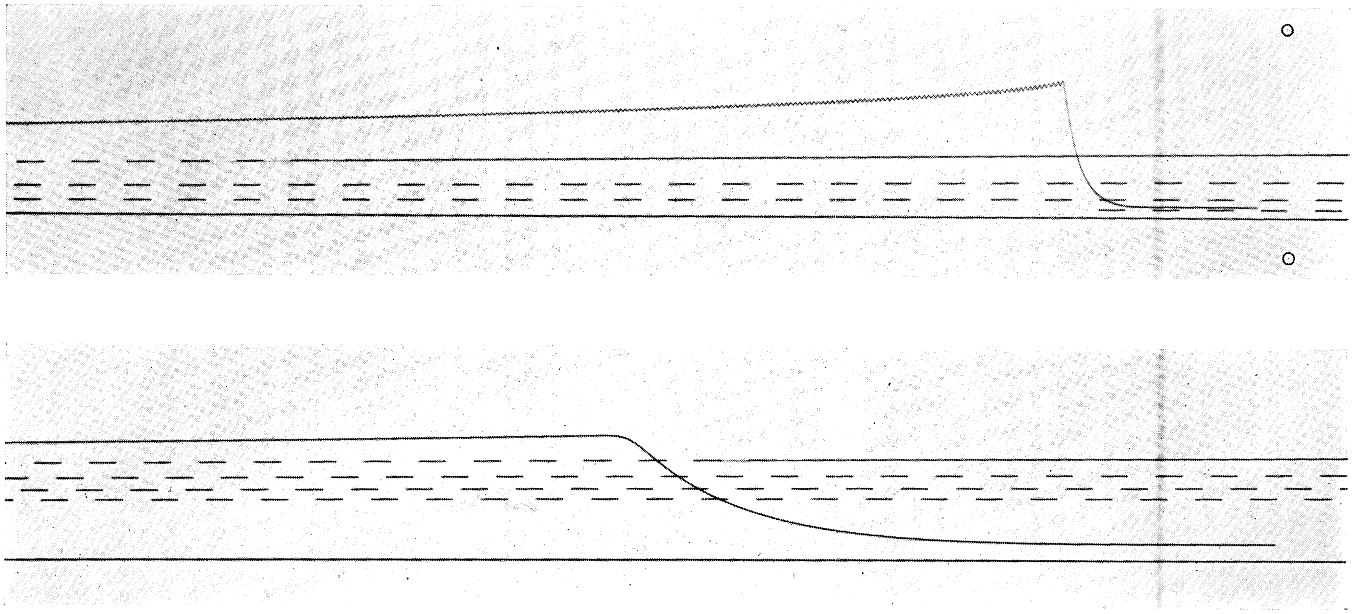


FIG. 3. Cage and top half of explosion vessel. The internal surface of the vessel has been dulled.



Upper record 519, mixture S 92: $P_i = 3{\cdot}007$ atm., $P_m = 22{\cdot}57$ atm., explosion time $= 0{\cdot}0186$ sec.
Lower record 280, mixture S 56*d*: $P_i = 3{\cdot}610$ atm., $P_m = 20{\cdot}66$ atm., explosion time $= 0{\cdot}103$ sec.

FIG. 18. Portions of typical explosion records.

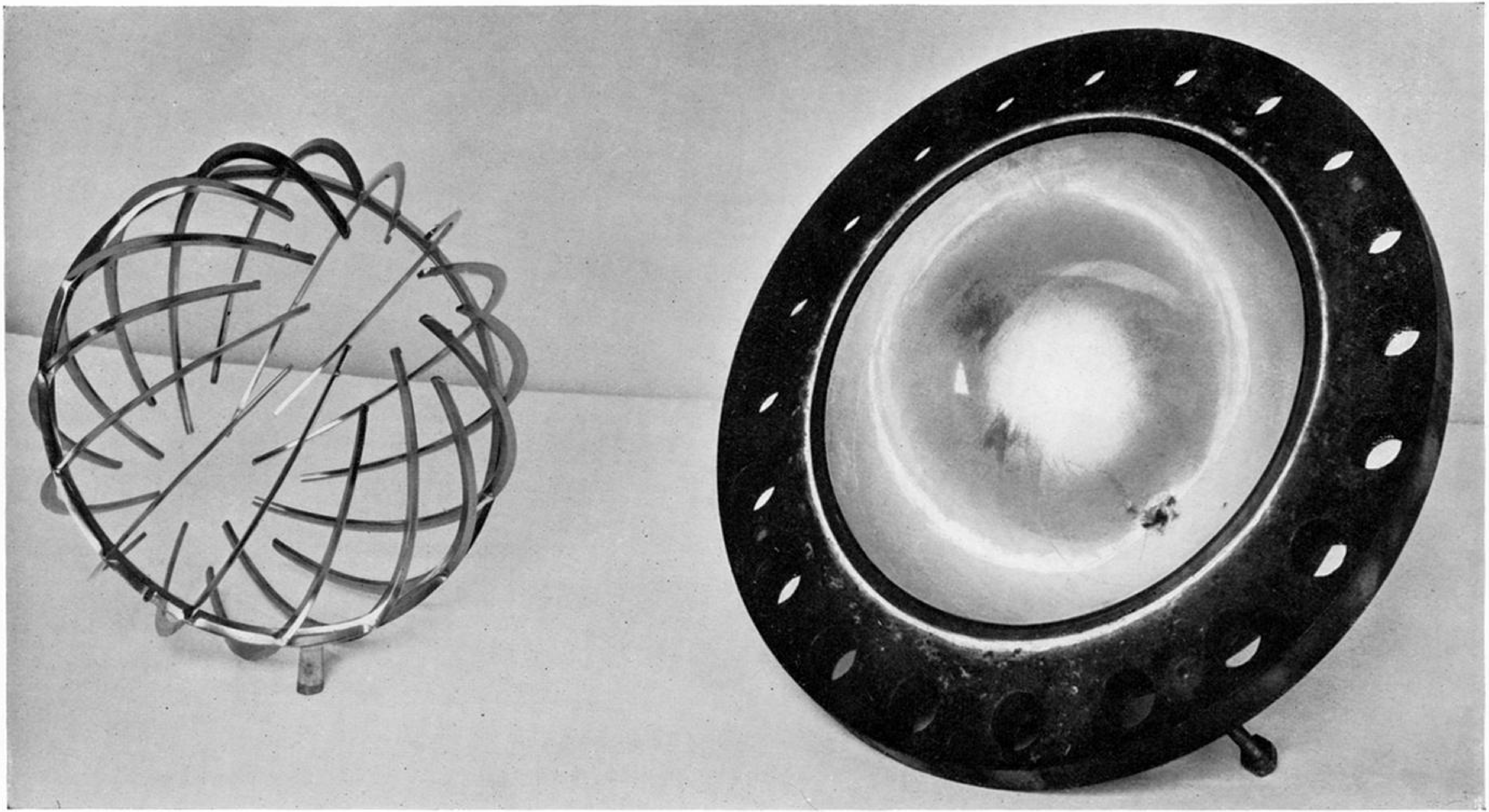
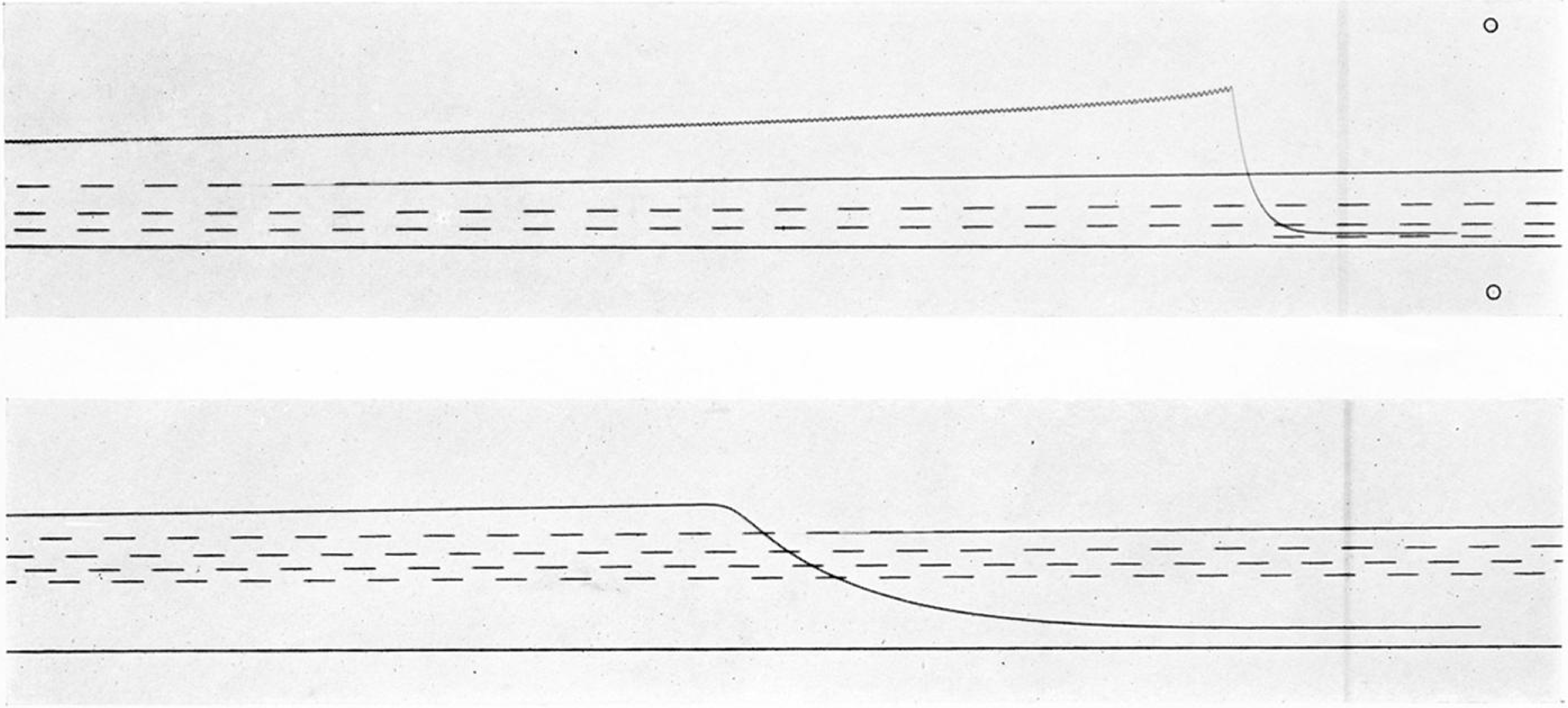


FIG. 3. Cage and top half of explosion vessel. The internal surface of the vessel has been dulled.



Upper record 519, mixture S 92: $P_i = 3{\cdot}007$ atm., $P_m = 22{\cdot}57$ atm., explosion time $= 0{\cdot}0186$ sec.
Lower record 280, mixture S 56*d*: $P_i = 3{\cdot}610$ atm., $P_m = 20{\cdot}66$ atm., explosion time $= 0{\cdot}103$ sec.

FIG. 18. Portions of typical explosion records.