

that it should always be considered as a possible factor in any theory of long distance propagation, as, if present, small changes in it may have very large effect on the signal intensity ; a wave with its electric vector horizontal having no effect whatever on normal receiving apparatus.

This work described was carried out as part of the programme of the Radio Research Board and is published by permission of the Department of Scientific and Industrial Research.

Finally, I must express my sincere gratitude to my colleague Mr. Naismith, both for his suggestion and carrying out of the original experiment which led to the work being undertaken ; and also for his share in the construction of the apparatus and in the taking of the observations ; involving as this does protracted and delicate observations over periods of several hours at all times of day and night.

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*Gaseous Combustion at High Pressures.—Part X. The Co-volume Corrections, Maximum Temperatures and Dissociation of Steam and Carbon Dioxide in Explosions.*

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*Introduction.*

During the researches upon high-pressure explosions of carbonic oxide-air, hydrogen-air, etc., mixtures, which have been described in the previous papers of this series, a mass of data has been accumulated relating to the influence of density and temperature upon the internal energy of gases and the dissociation of steam and carbon dioxide. Some time ago, at Prof. Bone's request, the author undertook a systematic survey of the data in question, and the present paper summarises some of the principal results thereof, which it is hoped will throw light upon problems interesting alike to chemists, physicists and internal-combustion engineers.

The explosion method affords the only means known at present of determining the internal energies of gases at very high temperatures, and it has

been used for this purpose for upwards of 50 years. Although by no means without difficulties, arising from uncertainties of some of the assumptions upon which it is based, yet, for want of a better, its results have been generally accepted as being at least provisionally valuable. Amongst the more recent investigations which have attracted attention in this connection should be mentioned those of Pier, Bjerrum, Siegel and Fenning, all of whom worked at low or medium pressures.

The experiments upon which the present investigation is based have included hydrogen- or carbonic oxide-air, etc., explosions over a much wider range of initial pressures (namely, 3 to 175 atmospheres) than any previously; and new information may be deduced from them as to the effects of density and temperature upon both the internal energies of gaseous media and the dissociation of steam and carbon dioxide.

Whilst the experiments in question were in progress it was possible, on certain provisional assumptions which seemed reasonable, to estimate approximately the maximum temperatures actually attained in the various explosions as well as the dissociation of steam or carbon dioxide thereat; but not until the accumulated data could be reviewed as a whole, and some additional experiments also made to elucidate dissociation factors, could any final figures be deduced. For the purpose of this paper, such a revision of the previous estimates of maximum temperatures and dissociation has been carried out; and the figures now given may be regarded as replacing the previous ones, which will be indicated in the text. From these it will be seen that, speaking generally, whilst the revised figures for the maximum temperatures attained in theoretical hydrogen-air and carbonic oxide-air explosions do not differ materially from those previously estimated in cases where the initial pressure did not exceed 25 atmospheres, at all higher pressures the newer estimates are lower than the old, and the more so as the initial pressure increases. This circumstance is due to the fact that a co-volume correction is now made in respect of the maximum pressure obtained in each explosion.

In the previous papers\* the opinion had been expressed that, in the explosions referred to, the dissociation of steam at maximum pressure had been "practically negligible," and that that of carbon dioxide had been "fairly constant at about 5 per cent. throughout the whole series of our CO-air explosions." The revised figures now submitted generally confirm these estimates; those for steam show a 2.2 per cent. dissociation at an initial pressure of 3 atmospheres, diminishing regularly to 1.0 per cent. only as the initial pressure was

\* *E.g.*, Part V, 'Roy. Soc. Proc.,' A, vol. 108, p. 393 (1925).



raised to 175 atmospheres. The new  $\text{CO}_2$ -dissociation figures (which vary only between 4.7 and 5.6 per cent.) all closely agree with the previous estimates.

A remarkable feature of the observed explosion data, to which attention was specially directed at the time, was the fact that the "corrected"  $P_m/P_i$  ratios always increased with the initial pressure in an unexpectedly large degree, as the following figures will sufficiently indicate:—

Mixture.	$P_m/P_i$ (corrected).		
	$P_i = 3.$	$P_i = 75.$	$P_i = 150.$
$2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ .....	7.70	8.43	8.82
$2\text{CO} + \text{O}_2 + 4\text{CO}$ .....	8.00	9.48	10.16
$2\text{CO} + \text{O}_2 + 4\text{N}_2$ .....	7.80	9.14	9.76

It was suggested that possibly the explanation might lie "in the increasing opacity of the gaseous medium with pressure to the radiation emitted during the explosion," and undoubtedly this accounts for a substantial part of the effect. It is now shown that about 50 per cent. of it in the case of the CO explosions, and about 75 per cent. of it in the hydrogen explosions, may be ascribed to the co-volumes of the components of the gaseous media in question, and that the correction on this account is not only a function of the initial pressure but also of the maximum temperature attained in the explosion.

#### *Consideration of the Various "Corrections" to be Applied to the Observed Explosion Data.*

In carrying out such explosions, the principal observations made are (1) the initial firing pressure ( $P_i$ ), as indicated by a standard Bourdon gauge; (2) the time taken ( $t_m$ ) for the attainment of maximum pressure from the commencement of the pressure rise; (3) the maximum pressure ( $P_m$ ) attained; and (4) the rate of cooling after maximum pressure—the last three being read off from the actual pressure-time record obtained by means of the Petavel manometer and its optically recording adjuncts. For purposes of calculation and comparison of results amongst themselves, certain "corrections" should be applied to the so-observed values of  $P_i$  and  $P_m$  respectively; these "corrections" are briefly as follows:—

*Initial Pressure ( $P_i$ ).*—This should be corrected for deviations from Boyle's Law, because neither term in the PV product is independent of pressure. In

cases where  $P_i$  does not exceed 10 atmospheres, the correction is so small as to be practically negligible, but at all higher pressures it is not so. Moreover, although the compressibilities of all the individual components of an explosive mixture may be accurately known over a wide pressure-range at room temperature, the failure at high pressure of the Law of Partial Pressures precludes any calculation therefrom of the compressibility of the mixture, the isotherm of which must always be determined by direct measurements at the room temperature. Such direct measurements have always been made in conjunction with our explosion experiments by means of an apparatus specially designed for the purpose; and from such measurements the observed initial pressures have been corrected. Such corrections be it noted include changes in both the pressure and volume terms in the equation of state, and no other "correction" of  $P_i$  is necessary.

The actual compressibility factors experimentally determined and used in correcting the observed  $P_i$  values, in our experiments, are as follows:—

Mixture.	Observed $P_i$ in atmospheres.					
	10.	25.	50.	90.	120.	150.
$2H_2 + O_2 + 4N_2$ .....	0.9954	0.9938	0.9922	0.9858	0.9836	0.9815
$2CO + O_2 + 4CO$ .....	1.001	1.008	1.020	1.023	1.015	1.006
$2CO + O_2 + 4N_2$ .....	1.002	1.007	1.017	1.016	1.013	0.9974

*Maximum Pressure ( $P_m$ ).*—Two corrections may be considered here, namely:—

(a) In cases where the attainment of the maximum pressure in an explosion is practically instantaneous—say, as in our case, within a time not exceeding 0.005 second which is actually the "time period" ( $\theta$ ) of the Petavel gauge—it is assumed that the observed  $P_m$  is not appreciably affected by any cooling of the gaseous medium by the walls of the explosion vessel. When, however,  $t_m$  exceeds 0.005 second, an appropriate "cooling correction" is applied to  $P_m$  in respect of the time period by which  $t_m$  exceeds 0.005 second. This is always done in comparing the results of two or more experiments with different explosive mixtures, so as to eliminate the influence of observed variations in  $t_m$ . For in such cases it is the " $P_m$  corrected" values which are taken into account. When, however, it is desired to calculate from the observed  $P_m$  value the mean maximum temperature ( $T_m$ ) actually attained in a particular explosion, such "cooling correction" is not applied; in such cases, however,



it is necessary to allow for "dissociation," and to apply also a co-volume correction.

(b) In so calculating  $T_m$  at the observed  $P_m$  value in a particular explosion, an allowance for "dissociation" comes in in so far as it affects the observed  $P_m/P_i$  ratio in respect of the observed degree of dissociation. Thus, for example, supposing, as is the case of a theoretical CO-air mixture, there be a 5 per cent.  $\text{CO}_2$ -dissociation at  $P_m$ ; then, instead of the medium at  $P_m$  consisting of  $2\text{CO}_2 + 4\text{N}_2$ , it consists of  $1.9 \text{ CO}_2 + 0.1 \text{ CO} + 0.05 \text{ O}_2 + 4\text{N}_2$ , and the observed  $P_m/P_i$  ratio should be multiplied by 1.157 instead of by 1.166 to allow for the medium at  $P_m$  containing 6.05 instead of the 6.00 molecules in an undissociated medium.

(c) As in the case of  $P_i$ , the observed  $P_m$  value in an explosion should be corrected for deviations of the gaseous medium from Boyle's Law\* which, of course, cannot be directly measured. It is possible, however, to deduce from first principles on certain very probable assumptions the magnitude of the "correction" which should be applied in a particular case, provided that the maximum temperature attained in the explosion is known approximately. The procedure adopted will now be considered.

*Deduction of the Co-volume Correction at the Maximum Temperature in an Explosion.*

In applying any one of the numerous equations of state, *e.g.*, that proposed by A. Wohl† in 1914—who applied it satisfactorily to the isotherms of carbon dioxide and of other gases up to pressures of 1000 atmospheres at ordinary temperatures—

$$P = RT/(v - b) - a/[Tv(v - b)] + c/T^2v^3$$

it has generally been assumed that the  $b$  term (co-volume) is practically independent of temperature, at any rate up to  $300^\circ \text{C}$ . The temperature rise in our explosions is of the order of  $2000^\circ$  to  $3000^\circ \text{C}$ . and it is doubtful whether the constancy of  $b$  can be assumed over such a wide range, especially as the viscosity of a gas is known to increase with temperature between 100 and  $1000^\circ \text{C}$ . in a manner consistent with the assumption that its molecular diameter diminishes as the temperature rises. On applying Wohl's equation to our explosion results, on the assumption that the second and third term of the equation become negligible at the maximum temperatures concerned, and that

\* I have to thank Mr. H. T. Tizard, C.B., F.R.S., for a private communication pointing out the magnitude of the co-volume correction in this connection.

† 'Z. Phys. Chem.,' vol. 87, p. 1 (1914).

the value of  $b$  as determined at ordinary temperatures remained constant, the so "corrected"  $P_m/P_i$  ratios were found to decrease considerably as the initial pressure rose beyond 10 atmospheres. Thus, for example, in the case of our theoretical hydrogen-air explosions the so "corrected"  $P_m/P_i$  values worked out as follows:—

$P_i$	3	10	25	50	75	100	125	150	175 Atmospheres.
$P_m/P_i$	7.70	7.84	7.73	7.51	7.41	7.26	7.02	6.70	6.47

Such a result being manifestly impossible—for it is unthinkable that the maximum temperature attained in such an explosion would diminish as the density of the medium increases—it follows that the assumption as to the invariability of " $b$ " with temperature must be abandoned.

There are two alternative methods of calculating the change in the value of " $b$ " with temperature based upon the view that the space occupied by a molecule of gas is proportional to the third power of the effective molecular diameter.

According to Sutherland's formula, the molecule diameter ( $\sigma$ ) varies with the absolute temperature ( $T$ ) as follows:—

$$\sigma_T^2 = \sigma_\infty^2 (1 + C/T) \quad (1)$$

where  $\sigma$  is the molecular diameter corresponding to  $T$  and the constant  $C$  is proportional to the work done in separating two molecules, originally in contact, to an infinite distance apart.

The expression as applied to our present problem leads to the following equation for the variation of the co-volume with temperature:—

$$b_T = b_0 \left\{ \frac{1 + C/T}{1 + C/T_0} \right\}^{3/2} \quad (2)$$

It has also been found that in a large number of cases the change of viscosity of a gas with temperature is very nearly proportional to the  $n$ th power of the absolute temperature  $T$ , where  $n$ , on the assumption that the repulsive force between two molecules in collision is equal to  $\mu\sigma^{-s}$ , is given by

$$n = S + 3/2 (S - 1).$$

On this view, the co-volume at a temperature  $T^\circ$  is given by

$$bT = b_0 (T/T_0)^{-3/S-1}. \quad (3)$$

The use of equations (2) and (3) for the purpose of correcting the pressure ratios in our explosions lead to results which differ from one another by between 1 and 2 per cent. at the higher pressures. It has therefore been thought advisable to employ both methods, and to compare the values both of the  $P_m/P_i$  ratios and of the maximum temperatures so obtained.



The following values for the constants in equations (2) and (3) have been employed\* :—

Gas.	C.	S.
Steam .....	650	4.6
Carbon dioxide .....	274	5.2
Carbonic oxide and nitrogen .....	118	9.3

and the value of  $b_T$  for the gaseous products obtained in the explosions at the maximum temperature calculated therefrom.

Values of  $b_T$  calculated by means of equations (2) and (3).

Products from explosions of—	Value of $b_T$ at temperatures (abs.).				
	273°.	2500°.	2700°.	2900°.	3100°.
$2H_2 + O_2 + 4N_2$ { (2) .....	0.00160	0.000695	0.000688	0.000681	0.000674
(3) .....	0.00160	0.000597	0.000580	0.000560	0.000543
$2CO + O_2 + 4CO$ { (2) .....	0.00170	0.000743	0.000737	0.000733	0.000700
$2CO + O_2 + 4N_2$ { (3) .....	0.00170	0.000623	0.000607	0.000583	0.000567

The corrected values of  $P_m$  are obtained by substituting values for  $b_T$  in the equation

$$P_m \text{ corr'd.} = P_m \text{ obs. } (v - b_T)/v$$

where  $v = 1/P_1$ .

Employing this equation, the  $P_m/P_i$  ratios, corrected in respect of both  $P_m$  and  $P_i$  for "co-volume," become :—

	$P_m/P_i$ (corrected).								
$P_i$ (atmospheres) .....	3.	10.	25.	50.	75.	100.	125.	150.	175.
(1) $2H_2 + O_2 + 4N_2$ mixture									
Equation (2) .....	7.70	7.78	7.91	7.88	8.00	8.04	8.03	7.91	7.90
Equation (3) .....	7.70	7.85	7.93	7.92	8.05	8.11	8.14	8.05	8.09
(2) $2CO + O_2 + 4CO$ mixture									
Equation (2) .....	8.03	8.33	—	8.50	8.87	8.88	8.95	8.95	—
Equation (3) .....	8.03	8.40	—	8.56	8.99	9.02	9.14	9.19	—
(3) $2CO + O_2 + 4N_2$ mixture									
Equation (2) .....	7.13	7.44	7.62	7.74	7.87	8.02	7.96	8.06	8.06
Equation (3) .....	7.13	7.50	7.54	7.80	7.95	8.13	8.10	8.25	8.26

\* C. J. Smith, 'Proc. Phys. Soc.,' vol. 34, p. 155 (1922); 'Roy. Soc. Proc.,' A, vol. 105, p. 242 (1924); Jeans 'The Dynamical Theory of Gases,' 4th ed.

In applying the co-volume correction derived from either of the two formulæ in question, preliminary calculations showed that the corrected maximum temperatures in all the explosions at initial pressures between 10 and 175 atmospheres (the only ones that matter) would fall within the limits  $2500^{\circ}$  and  $3100^{\circ}$ . Between these two temperature limits the diminution in the co-volume constant  $b$  is no more than about 10 per cent.; therefore, in calculating the maximum temperature, first of all an approximate estimate was made of it, using an appropriate co-volume constant between  $2700^{\circ}$  and  $2900^{\circ}$ , and such preliminary estimate of the maximum temperature derived always came within  $100^{\circ}$  of the final value. A final calculation was now made using the co-volume factor corresponding with the so-estimated temperature.

In the cases of mixtures (1) and (2), no "cooling correction" is necessary, because in each case  $t_m$  did not exceed 0.005 second; but in the case of the theoretical CO-air mixture (3), where  $t_m$  increased from 0.07 second at  $P_i = 3$  atmospheres to 0.56 second at  $P_i = 175$  atmospheres, a cooling correction must be superposed on the co-volume corrected  $P_m/P_i$  values in cases where comparisons with other mixtures are instituted. With such cooling-correction so superposed, the completely corrected  $P_m/P_i$  values for the  $2\text{CO} + \text{O}_2 + 4\text{N}_2$  mixture become:—

		$P_m/P_i$ corrected for cooling and co-volume.								
$P_i$ (atmospheres).....		3.	10.	25.	50.	75.	100.	125.	150.	175.
Equation {	(2) .....	7.80	7.94	8.16	8.35	8.67	8.72	8.64	8.75	8.95
	(3) .....	7.80	7.95	8.17	8.38	8.72	8.79	8.73	8.88	9.10

It will thus be seen that, in the case of the theoretical hydrogen-air explosions, from 70 to 80 per cent. of the observed great increase in the  $P_m/P_i$  ratios as the initial firing pressure was progressively raised from 3 to 175 atmospheres may be accounted for by the probable increase in the co-volume factor  $b$  with temperature and pressure. In the case of both the theoretical CO-air and the  $2\text{CO} + \text{O}_2 + 4\text{CO}$  explosions, however, only about half of the observed increase could be so accounted for. The remainder is probably due to an increase in the opacity of the medium with pressure, a supposition for which the research as a whole has afforded considerable support.



*The Dissociation of Steam and Carbon Dioxide at the High Temperatures and Pressures attained in the Explosions.*

Having corrected the observed  $P_m/P_i$  ratio for deviations from Boyle's Law in the way described in the previous paragraphs, it remained to determine the "degree of dissociation" of steam or carbon dioxide at the maximum pressure in each explosion before the maximum explosion temperature could finally be deduced. For, if  $P_i$  and  $P_m$  are the respective initial and maximum pressures, after correction in each case for deviation from Boyle's Law but not for "cooling,"  $e$  the ratio of the number of molecules before firing and at  $P_m$ , respectively, and  $V$  the volume of the explosion vessel, then

$$T_m = T_i \times P_m V \cdot e / P_i V,$$

when  $T_m$  = the actual mean maximum temperature (abs.) attained in the explosion and  $T_i$  = the initial firing temperature (abs.). And, since  $V$  does not sensibly alter during the explosion, it may be said that

$$T_m = T_i \times P_m e / P_i.$$

*Some General Considerations.*—Before proceeding, however, to show how the factor  $e$  has been determined, it seems desirable to say something more about the physical condition of the gaseous medium during our explosions, all of which (it may be recalled) were carried out in spherical steel bombs with an explosion chamber of 240 c.c. capacity, ignition being effected by the electric glowing of a fine platinum wire at a position near the walls of the chamber opposite to the head of the Petavel recording manometer. It may be here said that experiments have shown that, so far as the observed  $t_m$  and  $P_m$  values are concerned, it matters not whether ignition of the charge is effected as described or at a position right up against the head of the Petavel gauge. At such high firing pressures as have been used in most of our experiments, "central-ignition" is impracticable for reasons which need not be discussed here; but, had it been practicable, the observed  $t_m$ 's would have been uniformly about two-thirds those obtained with the firing position actually employed. Obviously the  $t_m$  observed in any particular case must depend upon the shape and dimension of the explosion chamber, and to some extent also upon the firing position in it; but, so long as these factors remain the same throughout a series of experiments, the observed  $t_m$ 's are all comparable among themselves.

In all such explosions, a measurable time is required after ignition for the flame to spread throughout the gaseous medium and for the observed maximum pressure to be attained. Strictly speaking, probably at no time during an explosion is the gaseous medium absolutely homogeneous throughout, especially

as to temperature; nor can the "cooling effect" of the vessel walls ever be entirely eliminated. In general, however, the denser the medium exploded, the shorter is  $t_m$ , and the less the said "cooling effect." Indeed, the only exception to this rule found so far at initial pressures between 10 and 175 atmospheres is afforded by our CO-air mixtures, where  $t_m$  rapidly increases with the initial pressure, owing to "nitrogen-activation" coming in. And it is the speeding up of  $t_m$  and the minimising of "cooling effects," as well as the high medium density itself which make high-pressure explosions so valuable a means of exploring gaseous interactions at high temperatures and densities.

It should always be borne in mind that, in speaking of the "maximum" temperature or pressure attained in any explosion in a closed vessel, the *mean* condition of the gaseous medium as a whole at the moment when the manometer records the maximum effect is meant; hence, the nearer the medium to absolute homogeneity at such moment, the nearer will the observed mean maximum temperature or pressure approximate to the true maximum explosion condition. In a bomb of infinite size no such approximation to homogeneity could ever be postulated; and the employment of explosion chambers of dimensions greater than are necessary to minimise the "cooling effects" of the walls would seem to be disadvantageous. In the case of our bombs, however, the moderate size of the explosion chamber (240 c.c.), whilst sufficient (at all initial pressures above about 10 atmospheres) satisfactorily to minimise "cooling effects," ensured a high degree of homogeneity of the medium at the moment of maximum pressure.

Attention has already been directed to the absence of any sign of what has been termed "after-burning,"\*—as distinct from "dissociation" effects at maximum pressure—in any of our explosions where the initial pressure exceeded 10 atmospheres, although in explosions at lower initial pressures such signs were distinctly present. Indeed, speaking generally, the characters of the "differential" cooling curves after the attainment of maximum pressure in explosions where  $P_i = 10$  atmospheres seem decisive against the supposition of "after burning," as distinct from "dissociation." In this connection may be recalled the highly significant circumstance that in all the  $2\text{CO} + \text{O}_2 + 4\text{CO}$  explosions at initial pressures of 50 atmospheres and upwards, the mean rate of cooling of the medium during the 0.5 second immediately after  $P_m$  was always proportional to something between the third and fourth power (increasing with the density of the medium) of the absolute temperature, a result hardly compatible with any "after burning" in such cases.

\* 'Roy. Soc. Proc.,' A, vol. 105, p. 417 (1924).



*Experimental Determination of Dissociation of Steam and Carbon Dioxide in Theoretical H<sub>2</sub>-air and CO-air Explosions.*

*Dissociation of Carbon Dioxide.*—A large number of experiments have been made with the object of determining the degrees of dissociation of carbon dioxide at the maximum temperature and pressures attained in our various theoretical carbonic oxide-air explosions, which covered a very wide range of initial pressures. Two methods were available, namely, those used by N. Bjerrum and by Tizard and Fenning, respectively, and both have been employed.

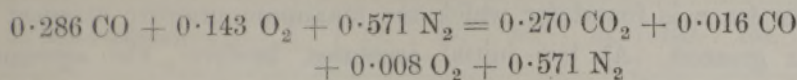
In Bjerrum's method, two mixtures are found at each required temperature, the one containing a large excess of the combustible gas and the other a corresponding excess of the nitrogen, such that on explosion the same maximum pressures are attained. Assuming that sufficient excess of combustible gas is present in the first mixture to suppress dissociation completely, the composition of the products of combustion of the second mixture may be calculated, and hence the percentage dissociation of the steam or carbon dioxide. Two further assumptions are made, namely (1) that the heat losses during explosion are the same for the two mixtures, and (2) that the specific heats of the two diatomic gases are identical at the high temperatures attained. The assumption as to equality of heat loss is only true when the explosion times of the two mixtures happen to be the same; consequently in finding corresponding mixtures the effect of differences in heat loss must be taken into account. The following example of the method, as applied to CO-air explosions, will perhaps suffice.

It had been previously found that the observed  $t_m$  and  $P_m/P_i$  ratio for a  $2\text{CO} + \text{O}_2 + 4\text{N}_2$  explosion at an initial pressure of 10 atmospheres were 0.10 second and 7.5 respectively.\* And, by interpolation from the results of the following further experiments upon  $2\text{CO} + \text{O}_2 + x\text{CO}$  mixtures at the same initial pressure (see Table I below), the "corresponding" carbonic oxide-oxygen mixture was found to contain 13.3 per cent. of oxygen and to have a  $t_m = 0.05$  second.

The difference between the "cooling losses" up to  $P_m$  in the two cases was estimated from the respective cooling curves as being 2 per cent.; therefore, the corresponding CO-O<sub>2</sub> mixture having the same cooling loss as the theoretical CO-air mixture at the said initial pressure is one containing 13.5 per cent. of oxygen, and giving on explosion a  $P_m/P_i$  value = 7.65. The carbon-

\* *Vide* Part V (*loc. cit.*), p. 406.

dioxide content of the exploded products of the two mixtures at the maximum pressure will be identical, so that at  $P_m$  in the CO-air explosion:—



from which it follows that, the “dissociation constant”

$$K_p = \left( \frac{0.016}{0.270} \right)^2 \times \frac{0.008}{0.865} \times 75 = 0.0024.$$

Accordingly, the percentage  $\text{CO}_2$ -dissociation at the observed maximum pressure of 75 atmospheres ( $T_m = 2505^\circ$  abs.) in the said theoretical CO-air explosion was 5.6 per cent.

Table I.—Showing Results of  $2\text{CO} + \text{O}_2 + x \text{CO}$  Explosions at  $P_i = 10$  Atmospheres.

Mixture.	$\text{O}_2$ -content.	$t_m$ .	$P_m/P_i$ obs.
	per cent.	second.	
$2\text{CO} + \text{O}_2 + 4\text{CO}$ .....	14.3	0.035	8.40
$2\text{CO} + \text{O}_2 + 5\text{CO}$ .....	12.8	0.060	7.18
$2\text{CO} + \text{O}_2 + 6\text{CO}$ .....	11.3	0.110	6.42

In a similar manner, the dissociation-constants of carbon dioxide at the observed maximum pressures and temperatures in our theoretical carbonic-oxide-air explosion at initial pressures of 50, 75, 100 and 125 atmospheres have been ascertained, with results as shown in the following table:—

Table II.

$P_i$ atmospheres.	Percentage $\text{O}_2$ -content of corresponding $\text{CO-O}_2$ mixtures.	$t_m$	$T_m$	$K_p$
		seconds.	$^\circ$ abs.	
10	13.50	0.05	2505	0.0024
50	13.61	0.05	2610	0.0083
75	13.62	0.06	2660	0.0120
100	13.53	0.05	2715	0.0230
125	13.57	0.05	2710	0.0250

The results so obtained by Bjerrum's method have been compared with those experimentally obtained by the method employed by Tizard and Fenning,



which consists in progressively increasing the amount of combustible gas in a  $2(1 + a)\text{CO} + \text{O}_2 + b\text{N}_2$  mixture (the ratio  $\text{N}_2/\text{O}_2$  being kept constant) until a value for  $a$  is found for which the maximum pressure attained on explosion is greatest. At low initial pressures, however, the agreement between the results of the two methods was not good, a circumstance probably due to the fact that, owing to the rather large surface volume ratio of our bomb, it is only at higher initial pressures that the two methods would be really comparable in our case. Also, the undoubted occurrence of a little "after burning" in our theoretical CO-air explosions at initial pressure up to (but not exceeding) 10 atmospheres would render the results of the two methods incomparable at such low pressures. The agreement between the results found by the two methods was, however, fair at an initial pressure of 50, and close at 125 atmospheres; but for the purpose of the calculations included in this paper, those obtained by the first (Bjerrum's) method have been adopted as the more reliable for our conditions.

The value of  $K_p$  so found for  $\text{CO}_2$ -dissociation over the temperature range  $2400^\circ$  to  $2800^\circ$  *abs.* may be represented by the empirical equation:—

$$\log K_p = 7.500 - 25,000/T.$$

Such  $K_p$  values, it may be noted, fall below those obtained by Bjerrum, but above those of Tizard and Fenning. Thus at  $2500^\circ$  *abs.*, whereas my values for  $K_p = 0.0024$ , according to Bjerrum it is 0.0040, and to Tizard and Fenning = 0.0011; again, whereas at a temperature of  $3200^\circ$  *abs.* Tizard and Fenning obtained  $K_p = 0.35$ , my value is 0.49, that of Bjerrum at  $3116^\circ$  being 0.70. Therefore, whilst agreeing with Tizard and Fenning's conclusion that Bjerrum's own estimations of  $\text{CO}_2$ -dissociation in CO-air explosions are probably too high, my experiments would show theirs to be rather too low.

From my so-experimentally determined values for  $\text{CO}_2$ -dissociation, the following contraction factors  $e$ , and maximum explosion temperatures ( $T_m$  *abs.*) have been deduced from the theoretical  $2\text{CO} + \text{O}_2 + 4\text{N}_2$  mixture when it was exploded in our experiments at various initial pressures between 3 and 175 atmospheres, the proper allowance having been made in each case in calculating  $T_m$  for all deviations from Boyle's Law both at  $P_i$  and  $P_m$ , respectively.

Table III.—Explosions of  $2\text{CO} + \text{O}_2 + 4\text{N}_2$  Mixture.

$P_i$ (atmospheres) .....	3.	10.	25.	50.	75.	100.	125.	150.	175.
$P_m/P_i$ corrected—									
Equation (2) .....	7.13	7.44	7.52	7.74	7.87	8.02	7.96	8.06	8.06
Equation (3) .....	7.13	7.50	7.54	7.80	7.95	8.13	8.10	8.25	8.26
$T_m$ absolute—									
Equation (2) .....	2385°	2485°	2505°	2590°	2630°	2680°	2665°	2695°	2700°
Equation (3) .....	2385°	2505°	2525°	2610°	2660°	2715°	2710°	2755°	2760°
Percentage $\text{CO}_2$ -dissociation at $T_m$ .....	5.1	5.5	4.7	4.9	4.9	5.4	5.0	5.6	5.3

Contraction factor  $\epsilon$  1.155 to 1.158.

Both  $P_i$  and  $P_m$  are corrected for deviation from Boyle's Law; but not  $P_m$  for "cooling," because it is the mean  $T_m$  actually attained in the explosion which is required.

It will be seen how very well the values for  $\text{CO}_2$ -dissociation so found agree with the estimate of a  $\text{CO}_2$ -dissociation "of the order of 5 per cent." in the said explosion previously given in Part V hereof (*loc. cit.*), pp. 410 and 417); the maximum temperatures actually attained in the various explosions as *then* and *now* compare as follows:—

Date.	$P_i$ (atmospheres).								
	3.	10.	25.	50.	75.	100.	125.	150.	175.
	°	°	°	°	°	°	°	°	°
Calculated $T_m$ in { 1925 .....	2393	2523	2573	2693	2793	2903	2943	3093	3143
{ 1928 .....	2385	2505	2525	2610	2660	2715	2710	2755	2760

Up to  $P_i = 25$  atmospheres the difference between the two sets of figures is not great; it is only at higher initial pressures, where the new "co-volume" correction at  $P_m$  comes in with increasing force as the density of the medium increases, that the differences become so.

In our  $2\text{CO} + \text{O}_2 + 4\text{CO}$  explosions, the combined effects of excess of combustible gas and high pressure are sufficient to suppress dissociation altogether; also the comparatively short  $t_m$ 's involve very small cooling corrections. The "corrected"  $P_m/P_i$  ratios for deviation from Boyle's Law both at  $P_i$  and  $P_m$ , and the  $T_m$  values calculated therefrom, are shown below:—



Table IV.—Explosions of  $2\text{CO} + \text{O}_2 + 4\text{CO}$  Mixtures.

		$P_i$ (atmospheres).						
		3.	10.	50.	75.	100.	125.	150.
$P_m/P_i$ corrected	{ Equation (2) .....	8.03	8.33	8.50	8.87	8.88	8.95	8.95
	{ Equation (3) .....	8.03	8.40	8.56	8.99	9.02	9.14	9.19
$T_m$ absolute	{ Equation (2) .....	2710°	2810°	2865°	2990°	2995°	3020°	3020°
	{ Equation (3) .....	2710°	2830°	2880°	3030°	3041°	3080°	3100°

These  $T_m$  values are all between  $270^\circ$  and  $370^\circ$  higher than in the corresponding  $2\text{CO} + \text{O}_2 + 4\text{N}_2$  explosions (*q.v.*) chiefly on account of the complete suppression of dissociation by the excess of combustible gas.

*Dissociation of Steam.*—Tizard and Fenning's method has been found quite reliable for deducing experimentally the  $K_p$  values for  $\text{H}_2\text{O}$ -dissociation in explosions of the theoretical  $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$  mixture at initial pressures of 50 and 125 atmospheres, respectively; but it is not so reliable at 10 atmospheres, for reasons already indicated. The experimental results (with  $P_i = 50$  and 125 atmospheres) which need hardly be detailed, are summarised in the curves (fig. 1) showing in each case the relations between  $P_m/P_i$  (ordinates) and percentage of hydrogen in the mixtures (abscissæ). Both curves show well

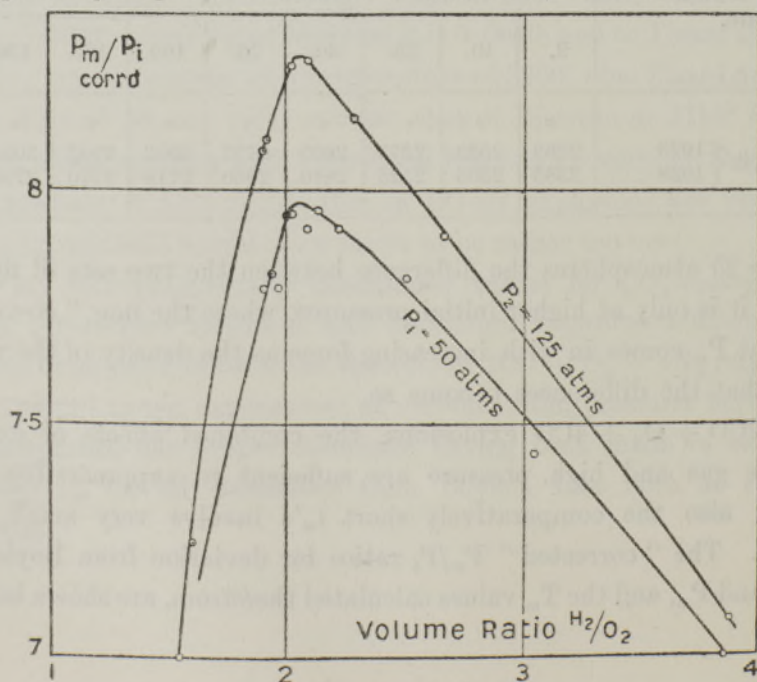


FIG. 1.

defined "maxima," with  $t_m = 0.005$  second in each case. The experimental details for the mixture giving the maximum  $P_m/P_i$  ratio at each initial pressure, are as follows :—

$P_i$ atmospheres.	$H_2/O_2$ ratio in mixture.	$a$ .	$P_m/P_i$ (corr'd.).	$T_m$ abs.	$x = a/b$ .	$K_p$ .
50	2.03	0.02	7.95	2682°	0.0053	0.00022
125	2.08	0.02	8.28	2800°	0.0053	0.00060

It may be remarked that the  $K_p$  values so ascertained agree very closely with those recently determined by W. Siegel,\* who found 0.00022 at 2602° and 0.00053 at 2800° abs.

On the foregoing basis, and correcting both the observed  $P_i$  and the  $P_m$  values for deviation from Boyle's Law (as already indicated) the following revised data for our theoretical hydrogen-air explosions at the various initial pressures have been deduced :—

Table V.—Explosions of the  $2H_2 + O_2 + 4N_2$  Mixtures.

$P_i$ (atmospheres) .....	3.	10.	25.	50.	75.	100.	125.	150.	175.
$P_m/P_i$ corrected—									
Equation (2) .....	7.70	7.78	7.91	7.88	8.00	8.04	8.03	7.91	7.90
Equation (3) .....	7.70	7.84	7.93	7.92	8.05	8.11	8.14	8.05	8.09
$T_m$ absolute—									
Equation (2) .....	2585°	2620°	2655°	2645°	2690°	2700°	2700°	2660°	2660°
Equation (3) .....	2585°	2640°	2660°	2665°	2710°	2730°	2740°	2710°	2715°
Percentage $H_2O$ -dissociation at $T_m$ .....	2.2	1.8	1.7	1.4	1.4	1.5	1.3	1.2	1.0

Previously, in Part V hereof (*loc. cit.*, pp. 398–400), on the basis of Nernst's figures, the  $H_2O$ -dissociation had been provisionally estimated as not exceeding 1.0 per cent.; it would now appear to vary continuously between 2.2 per cent. at the lowest and 1.0 at the highest initial pressure. And, as in the case of the theoretical CO-air explosions, the effect of the new "co-volume" correction for  $P_m$  now introduced has been to reduce materially the calculated  $T_m$ 's in all explosions where the initial pressure exceeded 25 atmospheres, as shown in Table on p. 480.

The progressive increase in maximum temperature with increase of density of the gas mixture is well illustrated by the curve in fig. 2 in which the temperatures plotted are those given by equation (3). It will be noticed that for the two

\* 'Z. Phys. Chem.,' vol. 87, p. 641 (1914).



Date.	$P_i$ (atmospheres).								
	3.	10.	25.	50.	75.	100.	125.	150.	175.
Calculated $T_m$ in $^{\circ}\text{C. abs.}$ —	o	o	o	o	o	o	o	o	o
1925 .....	2573	2623	2693	2733	2823	2893	2953	2963	3023
1928 .....	2585	2640	2660	2665	2710	2730	2740	2710	2715

carbonic oxide mixtures there is a rapid rise in the maximum temperature attained as the initial pressure is increased from 3 to 50 atmospheres, after

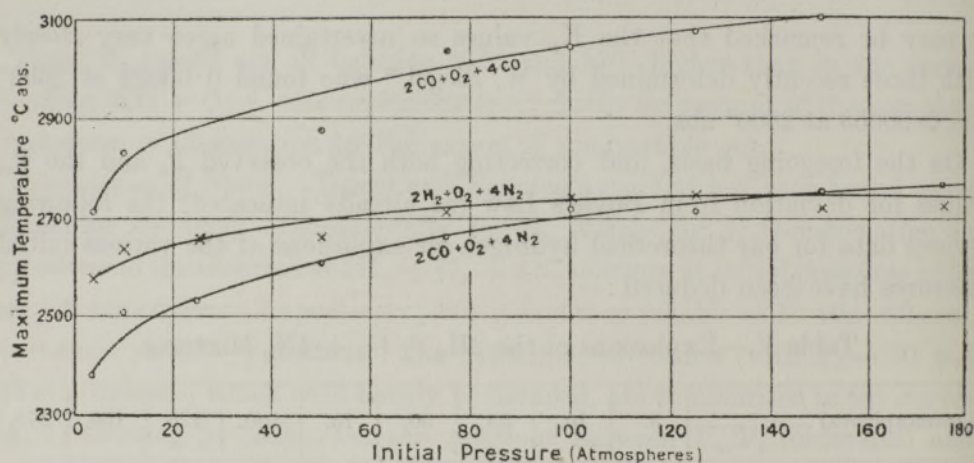


FIG. 2.

which the further increase is much slower and more uniform. The hydrogen-air mixture shows a similar (but not so rapid) rise in maximum temperature as the initial pressure increases from 3 to 50 atmospheres, which is followed by a period of fairly uniform temperature as the pressure increases to  $P_i = 175$ .

In conclusion, I desire to thank Prof. Bone for his constant interest and encouragement throughout my work and for placing all the resources of his laboratory at my disposal for it; also Prof. S. Chapman, of the Imperial College, and Mr. H. T. Tizard for advice in connection with particular matters upon which I have consulted them. Mr. C. M. Smith has also rendered me valuable assistance in connection with the new experimental work involved. Finally, my grateful acknowledgments are due to the Department of Scientific and Industrial Research for a personal grant which has enabled me to devote my whole time to this and cognate researches. The cost of the apparatus used has all been defrayed out of liberal grants placed at Prof. Bone's disposal by the Department of Scientific and Industrial Research and the Government Grant Committee of the Royal Society.