Method III (Iodide Method).—In this method the hypochlorite is reduced with potassium iodide. The mixture should be cooled in ice water before titrating with iodate. Chlorate interferes.

TABLE I

RESULTS

No.	NaClO by $Na_2S_2O_3$–I method, g.	NaClO by Method I, g.	NaClO by Method II, g.	NaClO by Method III, g.
1	0.0549	0.0545	0.0546	...
2	.0397	.0396	.0394	...
3	.0134	.0132	.0836	...
4	.0286	.0285	.0285	...
5	.0687	.0689	.0686	...
6	.0667	...	...	0.0664
7	.0694	...	...	.0693
8	.0675	...	...	.0672

Summary

Hypochlorite was determined by reducing with an excess of arsenite, thiosulfate or iodide and titrating the excess with iodate.

MADISON, WISCONSIN

THE GASEOUS EXPLOSIVE REACTION AT CONSTANT PRESSURE. THE EFFECT OF INERT GASES[1]

BY F. W. STEVENS

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Thermodynamics

The effect of inert gases upon the thermodynamic equilibrium of gaseous explosive reactions has received extended consideration from Nernst and his pupils,[2] who employed in their investigations a spherical bomb of constant volume with central ignition. This series of studies extended to temperatures of over 3000° Abs. and formed part of the most extensive investigation of gaseous reactions involving the equilibrium products of combustion, carbon dioxide and water vapor that has yet been carried out. "No other chemical equilibrium has so far been investigated by so many methods which can also be controlled at the same time by thermodynamic calculations. . . . A specially high value must be attached to explosion methods since by suitable variations of the experimental conditions it enables both the specific heats and the equilibrium to be determined."[3]

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[1] Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

[2] (a) Pier, *Z. Elektrochem.*, **15**, 536 (1909); (b) **16**, 897 (1910); (c) Bjerrum, *ibid.*, **17**, 731 (1911); (d) **18**, 101 (1912); (e) *Z. physik. Chem.*, **79**, 513, 537 (1912); (f) **81**, 284 (1913); (g) Siegel, *ibid.*, **87**, 641 (1914).

[3] Nernst, "Theoretical Chemistry," Macmillan Company, New York, 10th ed., 1923, p. 783.

The accuracy of explosion methods as employed by the investigators mentioned depends upon the favorable symmetry automatically assumed by the gross mechanism of the gaseous explosive reaction. The sharply localized zone of explosive reaction originating at the spark gap at the center of the spherical bomb is propagated in all directions from this point, as are also the sound and impulse waves resulting from it. Thus the zone of explosive reaction marked by flame and the disturbances and their reflections resulting from it, maintain during the reaction positions symmetrical with the spherical bomb. The equilibrium products of combustion thus remain enclosed within an expanding spherical shell of flame and are thereby protected as well as may be from heat losses due to the walls of the container till the end of the reaction and the attainment of maximum pressure. The maximum pressure of the equilibrium products filling the bomb at the instant the reaction is completed, corresponds to the equilibrium constant of the reaction

$$K = \frac{[\mathrm{A}']^{n'_1}\,[\mathrm{B}']^{n'_2}\,[\mathrm{C}']^{n'_3}\ldots}{[\mathrm{A}]^{n_1}\,[\mathrm{B}]^{n_2}\,[\mathrm{C}]^{n_3}\,\ldots.} \tag{1}$$

Pier[4] has shown that the deviation from this constant due to the presence of an inert gas permits the specific heat of that gas to be determined at reaction temperature; and Siegel[5] has shown that from a knowledge of the pressure of the bomb and the reaction constant the degree of dissociation of combustion products may be found. For example, in the case of the trimolecular explosive reaction, $2CO + O_2 \rightleftarrows 2CO_2$, Equation 1 may be written for constant volume conditions

$$K = \frac{[\mathrm{CO}]^2\,[\mathrm{O_2}]}{[\mathrm{CO_2}]^2} \tag{2}$$

and if x is the degree of dissociation of carbon dioxide, then

$$K = \frac{[\mathrm{CO}]^2\,[\mathrm{O_2}]}{[\mathrm{CO_2}]^2} = \frac{P}{2RT} \times \frac{x^3}{(1-x)^2\left(1+\dfrac{x}{2}\right)} \tag{3}$$

In a previous communication[6] a simple device was described that was found to function as a bomb of constant pressure; it thus provides the complement to the bomb of constant volume referred to above. It expresses the initial and final condition of the explosive reaction in terms of volume at constant pressure instead of pressure at constant volume. The thermodynamic relation between the two forms of device is expressed in the equation of state, $pv = nRT$.

Besides the advantages attending the use of constant pressure methods as applied to thermodynamic studies of gaseous explosive reactions, the experimental procedure in the use of the constant pressure bomb has the

[4] Ref. 2 a, p. 538.

[5] Ref. 2 g, p. 654.

[6] Stevens, THIS JOURNAL, **48**, 1896 (1926).

advantage of being unusually simple and direct. The labor and care necessary in evacuating and recharging a bomb of constant volume and of securing constant initial pressures and temperatures in the operations are tedious and time consuming. In the use of the constant pressure device and method these difficulties are practically eliminated. It is not difficult, using this device, to secure fifteen or twenty reaction records, giving initial and final volumes at constant pressure, within an hour. By securing so large a number of observations there is the advantage of using average results in computations.

The term volume here used in connection with the constant pressure bomb does not refer, as it does in the case of the constant volume bomb, to the actual volume of the temporary soap film container. The symmetry of form and movement automatically assumed by the reaction zone in the case of a homogeneous mixture of explosive gases fired from a point and under conditions of constant pressure, offers a much more accurate way of determining initial and final volumes involved in the transformation. The zone of explosive reaction originating at a point within a homogeneous mixture of explosive gases maintained at a constant pressure advances in all directions from this point at a constant linear speed. It thus forms an expanding spherical shell of flame that remains concentric with the point of ignition till the end of the reaction. This sphere of reaction products enclosed by the reaction zone is thus protected as well as may be from heat losses during the reaction, due to conduction and convection. By reference to Fig. 1 it will be seen that the initial volume of active gases whose transformation is photographically followed by the method used, is the volume of an ideal sphere $2r$ determined by the horizontal diameter of the container passing through the point of ignition and not the actual volume of the container itself, for this is never a sphere. The final volume is this initial volume transformed at a uniform linear rate into the sphere of equilibrium reaction products, $2r'$. The continuous volume changes during this reaction are recorded photographically together with time intervals of a calibrated fork.

The final volume represented by r'—as does the final pressure in the case of a constant volume bomb—corresponds to the equilibrium constant, K, of the reaction (Equation 1). Likewise the other thermodynamic relations characteristic of the reaction at constant volume conditions are expressible for conditions of constant pressure.

The conditions that determine uniform flame movement in a gaseous explosive reaction, whether for the slower reaction rates or for the more rapid rates of the Berthelot explosive wave, are a homogeneous mixture of the explosive gases and a constant pressure; for under these conditions only is it possible for the mass movement of the active gases and for their concentrations to remain constant during the reaction.

Kinetics

The photographic record (Fig. 1) of the gross mechanism and progress of the reaction at constant pressure, upon which equal time intervals have been impressed, is a time–volume record of the reaction and hence may provide some general information as to the kinetics of the gaseous explosive transformation.

If the rate of movement of the zone of explosive reaction is to be connected in any way with the rate of molecular transformation and hence with the rate of energy liberation, it is obvious that its rate should be determined relative to the active gases it is transforming and not relative to space. And it should likewise be recognized that unless the method employed makes it possible to follow the composition and concentrations of the active gases which the zone of explosive reaction is entering, a kinetic relation connecting the movement of the reaction zone with the composition and concentration of the explosive gases could hardly be expected to result from its use.

An examination of a great number of records similar to that reproduced in Fig. 1, obtained with different active gases at different concentration ratios, has shown that at constant pressure the rate of movement, s, of the zone of reaction, measured relative to the active gases, is constant and is proportional to the product of the initial concentrations (partial pressures) of those gases

$$s = k_1[\mathrm{A}]^{n_1}\ [\mathrm{B}]^{n_2}\ [\mathrm{C}]^{n_3}\ldots. \tag{4}$$

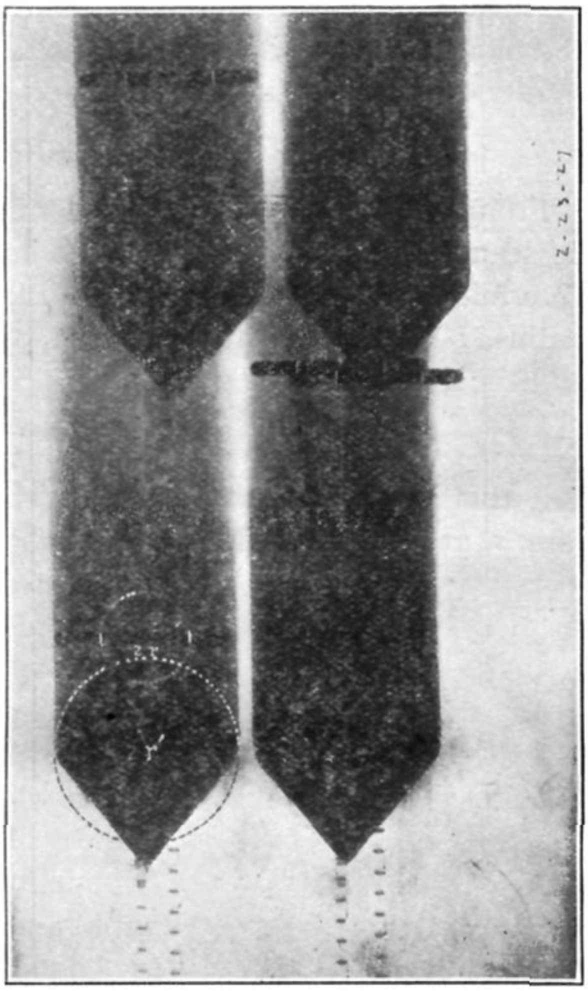

Fig. 1.—A reproduction of a photographic time–volume record of four gaseous explosions at constant pressure. $2r$ gives the dimensions of the sphere of initial active gases considered. $2r'$ the dimensions of the sphere of its reaction products at the instant the reaction is completed. Equal time intervals are recorded on the photographic film during the reaction process.

In this expression k_1 is a proportionality factor. The bracketed symbols represent initial concentrations or initial partial pressures of the active gases; their product expresses their impact probability, Γ; s is the linear rate of propagation of the reaction zone measured relative to the active gases it is entering.

It was of interest to examine the effect of inert gases on the rate of propagation of the zone of reaction in the light of the statistical relation expressed in (4) and by a method suggested by that employed by the investigators mentioned in determining the effect of inert gases upon the thermodynamic equilibrium. It is the purpose of this paper to record the results obtained in this endeavor.

Experimental Procedure

From the photographic figures of the progress of the reaction it will be seen that the constant rate of flame movement, s', in space may be determined at any instant during the transformation. It is equal to the radius, r'_i, at any instant divided by the time interval between ignition and the attainment of r'_i

$$s' = \frac{r'_i}{t} \qquad (5)$$

But this is not the rate at which the flame is entering the gases. The rate, s, at which the flame is entering the gases may be found for the case of a spherical shell of flame expanding at uniform rate s' as follows.

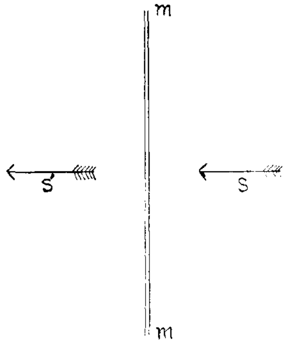

Fig. 2.

Let m, m, Fig. 2, be an element of the flame surface held at rest by the uniform flow s of the active gases against it; then s will be the rate at which the reaction zone enters the gases and s' will be the rate at which the transformed gases leave the flame area. If ρ and ρ' are the initial and final densities of the gases then from the equality of masses

$$\rho s = \rho' s' \qquad (6)$$

For the case of the initial and final spheres in the reaction, we also have from the equality of masses

$$\frac{4\pi\rho r^3}{3} = \frac{4\pi\rho' r'^3}{3} \qquad (7)$$

hence,

$$\frac{s}{r^3} = \frac{s'}{r'^3} \qquad (8)$$

$$s = s' \frac{r^3}{r'^3} \qquad (9)$$

For a test of these relations the gaseous explosive reaction at water vapor saturation

$$2CO + O_2 \rightleftharpoons 2CO_2 \qquad (10)$$

was selected. For this special case Equation 4 may be written

$$s = k_1[CO]^2\,[O_2] \qquad (11)$$

Including Equation 5

$$s = s' \frac{r^3}{r'^3} = k_1[\mathrm{CO}]^2\,[\mathrm{O_2}] \tag{12}$$

and

$$k_1 = \frac{r^3}{r'^2t\;[\mathrm{CO}]^2\,[\mathrm{O_2}]} \tag{13}$$

Since the sum of the partial pressures of the gaseous components present in the reaction at pressure p must equal p, Equation 11 may be written for atmospheric pressure

$$s = k_1[\mathrm{CO}]^2\,[1 - \mathrm{CO}] \tag{14}$$

without designating the composition of the term $[1-\mathrm{CO}]$ further than to indicate that the sum of the partial pressures of its components remains the same as the partial pressure of the component $[\mathrm{O_2}]$ in Equation 11; and that under the same circumstances the products $[\mathrm{CO}]^2\,[\mathrm{O_2}]$ and $[\mathrm{CO}^2]$ $[1-\mathrm{CO}]$ represent the same impact probability, Γ, though not the same proportion, k_1, of effective impacts nor the same potential energy. In case the component $[1-\mathrm{CO}]$ is made up of the fraction a of the active gas $\mathrm{O_2}$ and the fraction $1-a$ of some inactive gas, the partial pressure of the component $[1-\mathrm{CO}]$ may be expressed as

$$[1 - \mathrm{CO}] = \underset{\text{active}}{[1 - \mathrm{CO}]a} + \underset{\text{inert}}{[1 - \mathrm{CO}](1 - a)} \tag{15}$$

Equation 11 may then be written

$$s = k_1[\mathrm{CO}]^2\,[1 - \mathrm{CO}]a + k_1\,[\mathrm{CO}]^2\,[1 - \mathrm{CO}]\,(1 - a) \tag{16}$$

If, now, all of the impacts involving the inert gas are futile and the possible effect of its various physical properties, as specific heat, heat conductivity, etc., on the course of a thermal reaction be disregarded, then the last term in the above expression may be neglected and the effect on reaction probability of replacing the fraction $(1 - a)$ of an active gas by an inactive one be written

$$s = k_1[\mathrm{CO}]^2\,[1 - \mathrm{CO}]a \tag{17}$$

This expression takes into account the effect of the remaining active components only, and this is the major effect to be expected; but while the inert gas introduced may take no part in the molecular transformation, its presence in the zone of explosive reaction and in the active gases adjacent to it would naturally affect the heat distribution in that region. The effect of different inert gases upon the thermodynamic equilibrium is not the same; a quantitative estimate of their different effects permits their specific heats to be determined under the conditions resulting from the explosive reaction of the active gases. It might therefore be expected that the presence of inert gases in the zone of reaction would likewise have different effects upon the propagation of the reaction zone due to their individual characteristics.

In carrying out the observations the experiments were so arranged that the explosive transformation of the same partial pressures of the active gases, carbon monoxide and oxygen, could be observed on the same partial pressure of each of the inert gases used—and this over the entire range of mixture ratios of the gases that would ignite. The inert gases made use of were helium, argon, nitrogen and carbon dioxide. In the table below some of the physical properties of the gases involved in the transformations studied are set down. The values given for heat conductivity are taken from Taylor's "Treatise on Physical Chemistry," Vol. I, p. 92. The values for molecular heats are from Partington and Schilling, "Specific Heats of Gases."

TABLE I

MOLECULAR HEATS AND HEAT CONDUCTIVITIES OF GASES REFERRED TO IN THIS PAPER

Gas	He	A	N_2	O_2	CO	CO_2
Mol. heat	5.07	5.07	6.90	6.90	6.90	9.0
Heat conductivity	336.0	39.0	56.6	57.0	54.2	33.7

Table II, below, gives results obtained for the CO $-$ O_2 explosive reaction when no inert gas is present.

TABLE II

EXPERIMENTAL RESULTS OBTAINED FOR THE RATE OF FLAME PROPAGATION IN THE $2CO + O_2$ EXPLOSIVE REACTION AT CONSTANT PRESSURE

Record 9-7-27 No.	Partial pressure in atmospheres, [CO]	[O_2]	Γ $[CO]^2 [O_2]$	$s' = \frac{r_i}{t}$, cm./sec.	$s = s' \frac{r^3}{r'^3}$, cm./sec.	$k_1 = \frac{s}{\Gamma}$
1 to 3	0.224	0.776	0.0389	191	27.6	709
4 to 7	.260	.740	.0500	226	34.7	694
8 to 11	.279	.721	.0561	279	37.5	668
12 to 15	.310	.690	.0663	335	45.3	683
16 to 19	.325	.675	.0713	365	50.3	705
20 to 23	.359	.641	.0826	434	55.5	672
24 to 27	.388	.612	.0921	487	63.3	687
28 to 31	.416	.584	.1011	561	71.1	703
32 to 35	.460	.540	.1140	632	80.3	703
36 to 39	.491	.509	.1227	660	84.3	687
40 to 43	.523	.477	.1305	715	88.4	678
44 to 47	.574	.426	.1404	794	99.8	711
48 to 51	.622	.378	.1463	858	100.6	688
52 to 55	.688	.332	.1480	870	102.8	694
56 to 59	.726	.274	.1444	849	101.9	706
60 to 63	.775	.225	.1351	814	92.2	682
64 to 67	.810	.190	.1247	733	86.4	693
68 to 71	.840	.160	.1129	632	79.2	701
72 to 75	.848	.152	.1093	614	77.7	711
76 to 79	.883	.117	.0912	463	63.9	700
80 to 83	.903	.097	.0791	320	50.1	633
					Av. k_1	691

The results given in the above table may be expressed in graphic form by plotting the values of s as ordinates and either the corresponding partial pressures—shown in Fig. 3—or the corresponding values of $\Gamma = [CO]^2 [O_2]$, shown in Fig. 4 as abscissas. The method followed in Fig. 3 is the more familiar and will be used in expressing the results that follow. In Fig. 3 the observed values of $s = s'(r^3/r'^3)$ are represented by solid circles. Theoretical values of s, $s = k_1 [CO]^2 [O_2]$, are represented by open circles connected by a continuous line. This curve will be reproduced as a convenient reference in the other coördinate figures indicating the effect of inert gases on the CO − O_2 explosive reaction.

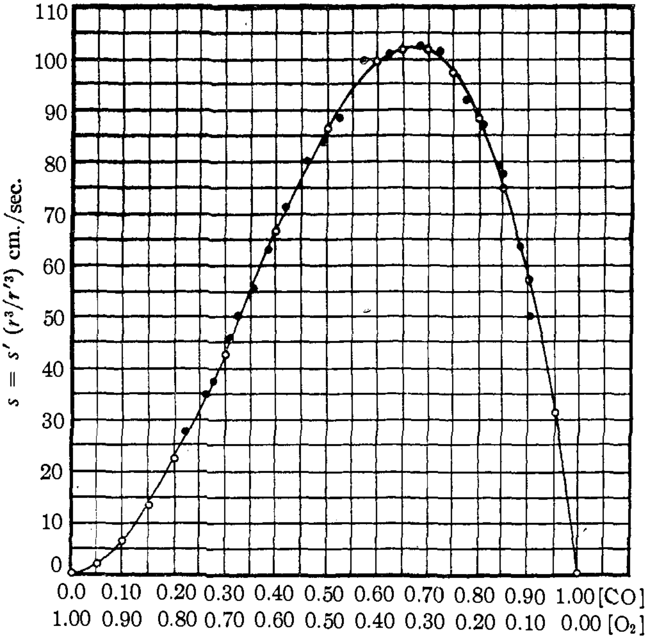

Fig. 3 shows the relation between the linear rate of propagation, s, of the zone of reaction, measured relative to the explosive gases, and the partial pressures of the gases, [CO] and [O_2], in the explosive mixture. The solid circles represent observed values, $s = s'(r^3/r'^3)$. The open circles and continuous line represent calculated values of $s = k[CO]^2 [O_2]$.

In Table III there are given the experimental results obtained when 10% of the component [1 − CO] consists of the inert gas A. These results are represented graphically in Fig. 5 by the mark ∨. The upper continuous curve in this figure gives velocity values of the reaction zone when no inert gas is present. The lower curve, indicated also by a continuous line, corresponds to Equation 17, $s = 691 [CO]^2 [1 - CO] 0.9$, for the case where 10% of the component [1 − CO] consists of an inert gas—

the possible effect of its physical properties being disregarded. There is also plotted on this figure the experimental values found when 10% of the

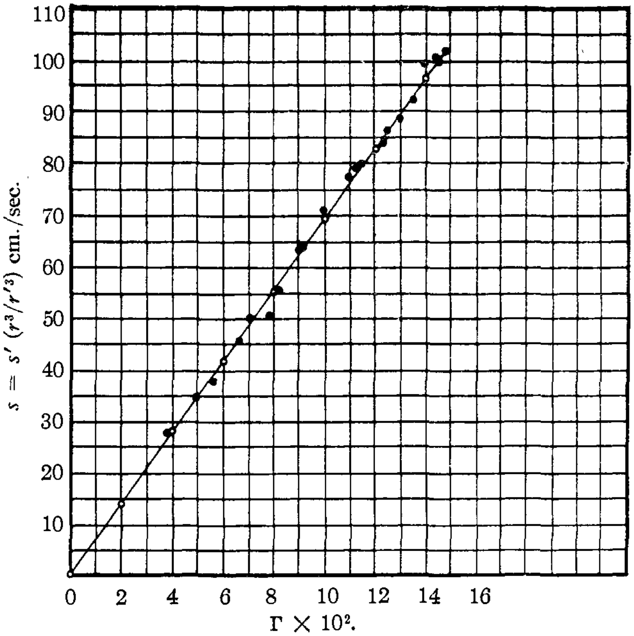

Fig. 4 shows the relation between the linear rate of propagation of the reaction zone, s, and impact probability, Γ.

component [1 − CO] consisted of nitrogen, marked × on the figure, carbon dioxide, marked ■, and helium marked ▲.

Table III

Experimental Results Obtained when 10% of the Component, [1 − CO] Consisted of the Inert Gas Argon

Record 5–28–28 No.	[CO]	Partial press., atm. [1 − CO]	[A]	Γ $[CO]^2 [1 - CO]$	$s' = \frac{r_i}{t}$, cm./sec.	$s = s' \frac{r^3}{r'^3}$, cm./sec.	$k_1 = \frac{s}{\Gamma}$
5 to 8	0.282	0.718	0.0718	0.0571	276	40.0	702
9 to 12	.326	.674	.0674	.0716	394	50.5	705
13 to 16	.373	.627	.0627	.0872	500	59.3	680
17 to 20	.426	.574	.0574	.1043	596	70.9	681
21 to 23	.472	.528	.0528	.1176	671	79.9	679
24 to 27	.521	.479	.0479	.1297	722	85.6	659
28 to 31	.572	.428	.0428	.1395	767	90.4	648
32 to 35	.625	.375	.0375	.1465	908	90.8	620
36 to 39	.674	.326	.0326	.1502	934	93.4	622
40 to 42	.726	.274	.0274	.1439	907	90.7	628
43 to 46	.775	.225	.0225	.1351	752	86.2	638
47 to 50	.824	.176	.0176	.1195	663	80.9	674
51 to 54	.876	.124	.0124	.0952	443	61.2	643

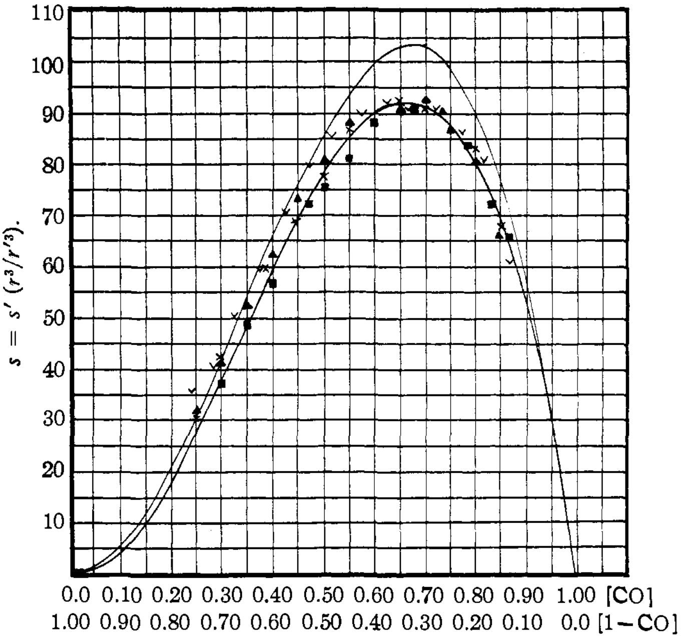

Fig. 5.—The upper continuous curve in this figure gives velocity values of the reaction zone when no inert gas is present. The lower curve, indicated also by a continuous line, corresponds to the equation, $s = 691\ [CO]^2[1-CO]\ 0.9$, for the case where 10% of the component [1−CO] consists of an inert gas, its possible physical effects being disregarded. The observed results when 10% of the component [1−CO] consisted of N_2 are indicated by the mark ×, A by the mark V, He by the mark ▲, and CO_2 by the mark ■.

Table IV

Experimental Results Obtained when 20% of the Component [1 − CO] Consisted of the Inert Gas Nitrogen

Record 4-22-27 No.	Partial press., atm. [CO]	[1 − CO]	$[N_2]$	Γ $[CO]^2\ [1 - CO]$	$s' = \frac{r_i}{t}$, cm./sec.	$s = s' \frac{r^3}{r'^3}$, cm./sec.	$k = \frac{s}{\Gamma}$
1 to 4	0.300	0.700	0.140	0.0630	245	36.2	575
5 to 9	.369	.631	.126	.0859	358	49.1	572
10 to 13	.420	.580	.116	.1023	440	58.2	569
14 to 17	.470	.530	.106	.1171	495	66.0	564
18 to 21	.521	.479	.096	.1300	581	73.2	563
22 to 25	.569	.431	.086	.1895	627	79.9	573
26 to 29	.616	.384	.077	.1457	651	82.8	592
30 to 33	.670	.330	.067	.1482	693	82.6	558
34 to 37	.718	.282	.056	.1453	666	81.8	563
38 to 41	.782	.218	.044	.1228	601	75.2	565
42 to 45	.822	.178	.036	.1203	529	65.2	542
46 to 49	.877	.123	.025	.0946	408	56.9	601

Table IV gives the experimental results when 20% of the component [1 − CO] was made up of the inert gas nitrogen. The observed values are indicated in the coördinate Fig. 6 by the mark ×. The upper continuous curve in this figure again represents velocity values of the reaction zone when no inert gas is present. The lower continuous curve in this figure corresponds to Equation 17, $s = 691\ [\mathrm{CO}]^2\ [1 - \mathrm{CO}]\ 0.8$. The observed results when the inert gas used was helium instead of nitrogen are represented by the mark ▲; when the inert gas was argon, by the mark V, and when the inert gas was carbon dioxide, by the mark ■.

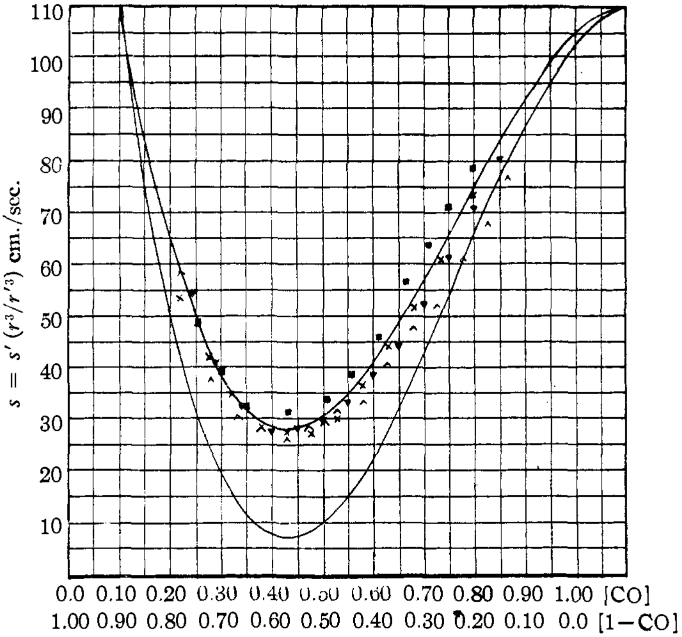

Fig. 6.—The upper continuous curve gives velocity values of the reaction zone when no inert gas is present. The lower continuous curve corresponds to the equation, $s = 691[\mathrm{CO}]^2[1 - \mathrm{CO}]0.8$; observed results when the inert gas present was N_2 are indicated by the mark ×, when the inert gas was He, by the mark ▲, A, by the mark V, CO_2, by the mark ■.

In Table V are given the experimental results obtained for $s = s'\ r^3/r'^3$ when 40% of the component [1 − CO] consisted of the inert gas helium. In Fig. 7 these results are shown graphically together with results obtained when the other inert gases were used in the same proportion. The marks employed to designate the s-values of the different inert gases in this figure are the same as those previously given.

From these results it may be seen that when small amounts (partial pressures) of different inert gases are present in the explosive mixture, not much difference in their individual effects is to be noticed; their different physical properties do not mask the effect of the active gases; but as the relative amounts (partial pressures) of the different inert gases become greater, a difference in their effect on the same $CO - O_2$ reaction becomes apparent. This is to be seen in the results given in Table V and shown in Fig. 7. The observed s-values not only diverge more widely from values indicated by Equation 17; they also differ characteristically from each other. It is further to be noticed that this divergence in each case is the greater, the greater the amount (partial pressure) is of the inert gas in the mixture. In Col. 4 of Table V is given the partial pressure of helium in each mixture ratio of [CO] and [1 − CO]. In Col. 8 of this table are given the corresponding values of $k_1 = s/\Gamma$. The values of k_1 in this

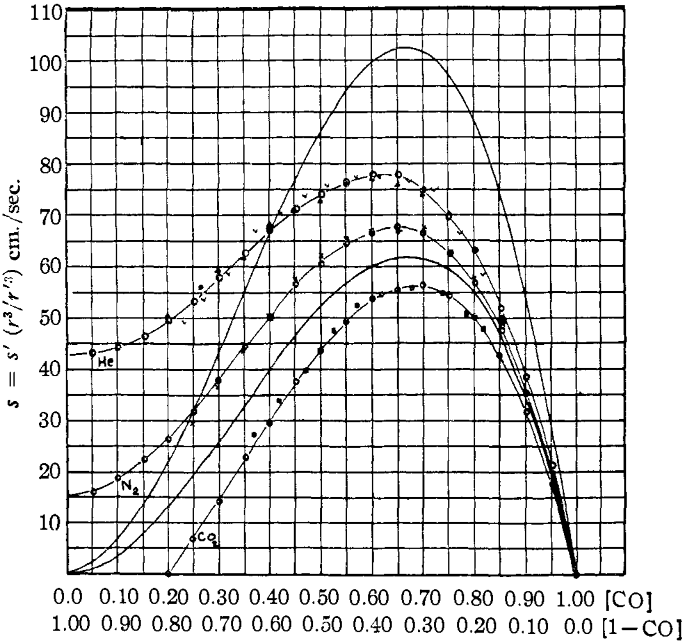

Fig. 7.—The upper continuous curve gives velocity values of the reaction zone when no inert gas is present. The lower continuous curve, without other marks, corresponds to the equation $s = 691 [CO]^2[1 - CO]$ 0.6, where 40% of the component [1 − CO] is made up of an inert gas whose effect upon the reaction rate is disregarded. Observed values when 40% of the component [1 − CO] consisted of A are marked ∨. Like values for N_2 are marked ×, He, ▲, and CO_2, ■. The curves in this figure marked He, N_2 and CO_2 shown by open circles and continuous lines correspond to Equation 18 when the experimental values for β found for the inert gases are introduced.

TABLE V

EXPERIMENTAL RESULTS OBTAINED WHEN 40% OF THE COMPONENT [1−CO] C
SISTED OF THE INERT GAS HELIUM

Record 2-5-27 No.	Partial press., atm. [CO]	[1 − CO]	[He]	Γ [CO]^2 [1 − CO]	$s' = \frac{rt}{t}$, cm./sec.	$s = s' \frac{r^3}{r'^3}$, cm./sec.	$k_1 = \frac{s}{\Gamma}$	$\beta =$ $s - k$ [CO] [1 − C [He
8′ to 11′	0.217	0.783	0.313	0.0369	262	49.5	1342	109
5′ to 8′	.265	.735	.294	.0516	339	56.1	1088	118
4 to 7	.302	.698	.279	.0637	376	59.9	940	120
8 to 11	.351	.649	.260	.0811	449	61.4	757	107
12 to 15	.400	.600	.240	.0960	498	68.0	708	117
16 to 19	.450	.550	.220	.1114	541	71.8	645	116
20 to 23	.500	.500	.200	.1251	567	72.3	578	102
24 to 27	.550	.450	.180	.1362	631	75.8	557	107
28 to 31	.600	.400	.160	.1441	613	76.5	531	105
32 to 35	.650	.350	.140	.1479	612	76.6	518	114
36 to 39	.700	.300	.120	.1470	591	73.9	503	108
40 to 43	.750	.250	.100	.1406	538	69.5	506	112
44 to 47	.800	.200	.080	.1280	446	61.3	479	102
48 to 51	.850	.150	.060	.1084	298	51.0	471	101
							Av. β =	109

column, according to the assumption made in Equation 17, should be c stant and equal to 415. • The values of k_1 are seen to be far from constan this case and only approach the theoretical value for no effect of an in gas as the partial pressure of helium in the mixture decreases. The high value of k_1 is seen to correspond to the greatest amount of helium in explosive mixture and *vice versa.*

It was conceived that the relationship shown in the table between values of helium and k_1 could be due to characteristic physical propert whatever they might be, of the inert gas present in the mixture and that magnitude of their different effects upon the CO − O_2 reaction might directly proportional to the partial pressure of the inert gas in the mixt that is

$$s = s' \frac{r^3}{r'^3} k_1 [\mathrm{CO}]^2 [1 - \mathrm{CO}] a + \beta [\mathrm{G_i}] \qquad (1$$

where $[\mathrm{G_i}]$ is the partial pressure of the inert gas. The observed res were examined for this relationship. The last column of Table V gi the estimated value of β for each mixture ratio of [CO] and [1−C that would ignite

$$\beta = \frac{s - k_1 a [\mathrm{CO}]^2 [1 - \mathrm{CO}]}{[\mathrm{He}]} \qquad (1$$

When the average value of β so found, 109, is substituted in Equation the curve represented by open circles and a continuous line, marked in Fig. 7, is determined. In a similar way it was found that the value

β for each of the other inert gases used was also a fair constant. Its value for 40% of N_2 in this reaction is 41, for CO_2, -41.8 and for A, 112.

In carrying out the experimental work involved in these studies, the inert gases helium, nitrogen and carbon dioxide were first employed. A comparison of the results obtained with these gases indicated that their effect upon the $CO - O_2$ reaction was of an order roughly paralleling the order of their heat conductivities, but following also the order of their molecular heats. It was therefore desirable to compare the effects of the two monatomic inert gases, helium and argon, having the same molecular heat but very different heat conductivities. A sample of argon was later obtained and the comparison made. The results indicate that the sample of argon used has practically the same effect on the rate of propagation of the reaction zone in the $CO - O_2$ explosive reaction as the inert gas helium. These two gases being monatomic have the same molecular heat independent of temperature, but the heat conductivity of helium is 8.6 times that of argon.

The mixture ratio for maximum flame velocity for the conditions expressed by Equations 14 and 17 is that given by position 0.667 in the coördinate figures; but for Equation 18 this position will be displaced to the left according to the positive magnitude of the last term, and to the right according to its negative magnitude. This may be seen in the results given in Fig. 7. It is also of interest to note that it might be possible to have a mixture of two inert gases whose individual effects upon the rate of propagation of the reaction zone were in opposite sense and balanced each other. For such a case the last term in Equation 18 would be negligible. The conclusion could be drawn from a special case of this kind that the rate of propagation of the zone of reaction is proportional to the product of the concentrations of the active components as in the case of the pure gases $CO–O_2$. This conclusion might also seem warranted from experimental results obtained when the inert gas is present in the explosive mixture in comparatively small quantities as shown in Figs. 5 and 6 and for all results where the value of $[CO]$ is large and the partial pressure of the inert gas small. It was therefore essential in carrying out the investigation to determine in each case the effect of the same partial pressure of each of the inert gases on the same mixture ratio of $[CO]$ and $[1-CO]$, and this over the entire range of mixture ratios that would ignite. In Fig. 7 the results of this procedure when 40% of the component $[1-CO]$ consists of an inert gas is shown for the inert gases helium, argon, nitrogen and carbon dioxide.

The writer desires to express here his gratitude to the National Advisory Committee for Aeronautics for interest, encouragement and support extended him during an investigation of gaseous explosive reactions. This report deals with the effect of inert gases on the reaction.

Summary

1. Attention is called to previous investigations of gaseous explosive reactions carried out under constant volume conditions, where the effect of inert gases on the thermodynamic equilibrium was determined. The advantage of constant pressure methods over those of constant volume as applied to studies of the gaseous explosive reaction is pointed out and the possibility of realizing for this purpose a constant pressure bomb mentioned.

2. The application of constant pressure methods to the study of gaseous explosive reactions made possible by the use of a transparent constant pressure bomb, led to the discovery of an interesting kinetic relation connecting the rate of propagation of the zone of explosive reaction within the active gases, with the initial concentrations of those gases

$$s = k_1[A]^{n_1}\ [B]^{n_2}\ [C]^{n_3}\ldots.$$

3. By a method analogous to that followed in determining the effect of inert gases on the equilibrium constant K, the present paper records an attempt to determine their kinetic effect upon the expression given above. It is found that this effect on the $CO - O_2$ reaction for the inert gases investigated, helium, argon, nitrogen and carbon dioxide, may be expressed as

$$s = k_1[A]^{n_1}\ [B]^{n_2}\ [C]^{n_3}\ldots.\ +\beta[G_i]$$

where $[G_i]$ represents the initial concentration of the inert gas in the mixture.

4. An example of the utility of the constant pressure bomb for the study of the kinetics of the gaseous explosive reaction is offered in the results given in the present paper.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

THE EQUILIBRIUM OF SILVER OXIDE AND SILVER CHLORIDE WITH AQUEOUS POTASSIUM CHLORIDE AND POTASSIUM HYDROXIDE

BY ROY F. NEWTON

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Lewis and Randall,[1] in one of their calculations of the free energy of formation of water, have made use of Noyes and Kohr's[2] measurements on the equilibrium between silver oxide, silver chloride, potassium hydroxide, potassium chloride and water. They point out that it would be much simpler to use the dissociation of silver oxide into silver and oxygen, and the electromotive force of a silver–silver oxide electrode against the hydrogen electrode, but that the silver–silver oxide electrode is quite variable

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, New York, 1923, p. 482.

[2] Noyes and Kohr, *Z. physik. Chem.*, **42**, 336 (1902).