

THE COMBINATION OF CARBON MONOXIDE AND OXYGEN
UNDER THE INFLUENCE OF RADON*

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The observations of Lind and Bardwell¹ showed that in many cases where an inert gas is present with one or more reactants in a gaseous system exposed to the alpha radiation from radon contained in the mixture, the rate of reaction is proportional to the total ionization produced in the system including that on the inert gas. This raised the question as to why carbon dioxide had not appeared to exert a similar influence on the oxidation of carbon monoxide² previously investigated.

In the present work, carbon dioxide has been added to a stoichiometric mixture of carbon monoxide and oxygen, equal to the amount of carbon dioxide that could be finally produced in the completed reaction. The rate of reaction in this mixture was compared experimentally with the rate of a mixture of carbon monoxide and oxygen of the same partial pressures, but without any initial carbon dioxide, when brought about by the alpha radiation from the same amount of radon in both cases.

To anticipate the conclusion of the investigation, it may be stated that carbon dioxide has been found to exert a positive influence on the rate of reaction, but one which is small relative to that which it would have exerted had all of the ions produced on it been equally effective with those produced in the reacting gases. Instead of the ions of carbon dioxide being found 100% efficient in promoting the oxidation of carbon monoxide, the experiments enable the assignment to carbon dioxide of a rather definite efficiency of only 14.5%. This small efficiency explains the failure to detect it in the earlier experiments since there appears to have been a compensation of two oppositely directed influences, the first half of the reaction beginning with abnormally high velocity which diminishes to a minimum about midway in the reaction, from which point a gradual rise takes place that is no doubt due to the accumulation of carbon dioxide in the system. Therefore, the introduction of a large amount of initial carbon dioxide has brought its accelerating influence into greater prominence.

Experimental.—The experiments consisted in following the reactions manometrically in spherical vessels using the general methods that have been employed in the work already cited. The reaction vessels were kept in a thermostat at 25°C. The mercury manometer levels were read with the aid of a cathetometer.

Customary methods were used for the preparation, purification and analysis of the gases. Carbon monoxide was prepared by the action of

formic acid on concentrated sulphuric acid; oxygen, by heating a 3:1 mixture of potassium permanganate and barium peroxide; and carbon dioxide, by heating sodium bicarbonate, from which the 2:1 carbon monoxide-oxygen mixtures were prepared. The stock mixtures were shown by explosion to contain more than 99.5% of the stoichiometric mixtures. The carbon dioxide used was better than 99.6% pure, while the carbon monoxide and oxygen were over 99.7% pure.

TABLE I
THE CARBON MONOXIDE OXIDATION BY RADON

EXPT. 1. $2\text{CO}(\text{g}) + 1\text{O}_2(\text{g}) = 2\text{CO}_2(\text{g})$				EXPT. 2. $2\text{CO}(\text{g}) + 1\text{O}_2(\text{g}) + 2\text{CO}_2(\text{g}) = 4\text{CO}_2(\text{g})$			
$D = 1.877 \text{ CM. } E_0 = 50 \text{ MC. RN}$				$D = 1.904 \text{ CM., INITIAL } P_{\text{CO}_2} = 418.7 \text{ MM.}$			
P_{total} MM.	$P_{2\text{CO}+1\text{O}_2}$ MM.	$P_{\text{CO}_2}^i$ MM.	$e^{-\lambda t}$	P_{total} MM.	$P_{2\text{CO}+1\text{O}_2}$ MM.	$P_{\text{CO}_2}^i$ MM.	$e^{-\lambda t}$
629.7	629.7	0	1.0000	1035.4	618.2	418.7	1.0000
617.9	594.6	23.4	0.9765	1021.7	577.1	446.1	0.9759
608.3	565.8	42.6	0.9524	1010.8	544.4	467.9	0.9512
597.8	534.4	63.5	0.9220	998.8	508.5	491.8	0.9208
586.9	501.7	85.3	0.8869	970.2	423.0	548.8	0.8416
573.4	476.4	102.2	0.8431	948.7	358.8	591.6	0.7750
554.3	404.4	150.2	0.7778	933.8	314.4	621.2	0.7100
539.0	358.8	180.6	0.7100	912.4	250.8	663.7	0.6235
522.4	309.3	213.6	0.6242	894.0	196.1	700.1	0.5207
504.5	256.0	249.1	0.5214	871.5	129.3	744.6	0.3834
483.6	193.9	290.5	0.3839	857.8	88.7	771.7	0.2926
471.7	158.7	314.0	0.2929	843.0	44.9	800.9	0.1534
461.7	129.0	338.8	0.2174				
454.2	106.8	348.6	0.1538				

$$\frac{(E_0)_2}{(E_0)_1} = 1.048$$

* Pressures of CO_2 corrected to ideal gas behavior.

In table 1 are given the results of experiments 1 and 2, the latter being the catalyzed reaction. Here, and in subsequent tables, pressures are calculated for 0°C . Correction is made for the non-ideal behavior of carbon dioxide.

The fact that experiment 2 with initial carbon dioxide present is proceeding faster than experiment 1 can best be shown by plotting the values of $\log P_{(2\text{CO}+1\text{O}_2)}$ as ordinates against $e^{-\lambda t}$ as abscissae in which $e^{-\lambda t}$ is the usual expression for logarithmic decay of radon. The results of this plot are shown in table 2 in the form of a catalytic factor by which is meant the ratio of the velocity of the reaction with initial carbon dioxide $\left(\frac{k\mu}{\lambda}\right)'_c$ to that without $\left(\frac{k\mu}{\lambda}\right)'$. In table 2 the catalytic factor³ appears as the ratio of the slope of experiment 2 to the slope of experiment 1 after making slight

corrections for the difference in diameter of the reaction spheres⁴ and for small differences in the quantities of radon employed.

TABLE 2
CATALYTIC FACTORS

$e^{-\lambda t}$	SLOPES OF LOG $P^{2\text{CO}+10\text{r}}$ VS. $e^{-\lambda t}$ CURVES			CATALYTIC FACTORS
	EXPT. 2	EXPT. 1	$\frac{\text{SLOPE OF 2}}{\text{SLOPE OF 1}}$	
1.0	1.415	1.044	1.355	1.331
0.9	0.974	0.794	1.227	1.205
0.8	0.974	0.794	1.227	1.205
0.7	1.016	0.782	1.300	1.276
0.6	1.058	0.777	1.361	1.336

$$\frac{D_2^2}{D_1^2} \div \frac{(E_0)_2}{(E_0)_1} = 0.892$$

Kinetic Equation for Efficiency Factor.—The general kinetic equation to express the velocity of a reaction proceeding under the influence of radon⁵ is

$$\text{const.} = \left(\frac{k\mu}{\lambda}\right)' = \frac{2.303 \Delta \log P_t}{E_0 \cdot \Delta e^{-\lambda t}}, \quad (1)$$

in which P_t is the variable partial pressure of the reactant gas at any time t , E_0 is the initial radon in the system and $\left(\frac{k\mu}{\lambda}\right)'$ is a velocity constant which for any given experiment has the dimensions of amount of reaction per 1 curie of radon. In the case of the presence of a foreign gas, the ions of which contribute to the reaction rate with 100% efficiency, Lind and Bardwell⁶ developed the equation:

$$\left(\frac{k\mu}{\lambda}\right)' = \frac{2.303 \Delta \log \left(P_t + \frac{i_c}{i} P_c\right)}{E_0 \Delta e^{-\lambda t}} \quad (2)$$

in which i_c is the relative specific ionization of the inert (catalytic or sensitizing) gas, i is the specific ionization of the reactant or mixture of reactant gases, and P_c is the partial pressure of the inert gas. The term $\frac{i_c}{i} \cdot P_c$ is the equivalent pressure of reactants in which the same ionization would be produced by radon as in the reactants themselves at this same pressure. Therefore, the sum of the equivalent pressure and actual pressure of reactants is proportional to the ionization that would be produced in this total pressure of reactants under the same conditions, assuming 100% catalytic efficiency of the ions of the chemically inert gas.

In the present work, however, it is found that the efficiency is only $x\%$, and therefore a new expression is used:

$$\left(\frac{k\mu}{\lambda}\right)_{\text{corr}} = \frac{2.303 \Delta \log \left(P_t + x \frac{i_c}{i} \cdot P_c \right)}{E_0 \Delta e^{-\lambda}} \quad (3)$$

in which the term $x \frac{i_c}{i} \cdot P_c$ gives the reduced ionic equivalent. For the case of carbon dioxide influencing the carbon monoxide oxidation, the value of P_{CO_2} is variable with time since CO_2 is produced by the reaction. To determine the value of x for carbon dioxide by a trial and error method would be extremely laborious and uncertain. However, the definition of the catalytic factor permits a simple experimental determination of the efficiency of carbon dioxide as a catalyst or sensitizer.

After having reduced the velocity constants to a common basis of equal spherical volume in the two cases and furthermore by considering equal time intervals so that the decay constant cancels out, we may write:

$$[\Delta \log P_{(2\text{CO}+1\text{O}_2)}]_{\text{catalyzed}} = \text{constant} \times [\Delta \log P_{(2\text{CO}+1\text{O}_2)}]_{\text{normal}} \quad (4)$$

from which the course of one reaction may be predicted from that of the other if the catalytic factor is known. Since the initial $P_{(2\text{CO}+1\text{O}_2)}$ is not identical for both reactions of the pair but differs by a few millimeters, we may calculate exactly the pressures in either reaction from the corresponding pressures in the other by applying equation (4). Table 3 shows this calculation. Pressures for the first parts of experiment 2 are computed on the basis of interpolated values of $\log P_{(2\text{CO}+1\text{O}_2)}$ from the normal reaction at rounded values of $e^{-\lambda}$.

TABLE 3
THE CARBON MONOXIDE OXIDATION AT ROUNDED VALUES OF $e^{-\lambda}$

$e^{-\lambda}$	CATA- LYTIC FAC- TOR	AVER- AGE FAC- TOR	EXPERIMENT 1				EXPERIMENT 2	
			LOG $P_{(2\text{CO}+1\text{O}_2)}$	LOG $P_{(2\text{CO}+1\text{O}_2)}$	Δ LOG $P_{(2\text{CO}+1\text{O}_2)}$	Δ LOG $P_{(2\text{CO}+1\text{O}_2)}$	LOG $P_{(2\text{CO}+1\text{O}_2)}$	LOG $P_{(2\text{CO}+1\text{O}_2)}$
1.0	1.331		629.7	2.7991			2.7991	629.7
		1.268			0.0882	0.1118		
0.9	1.205		513.9	2.7109			2.6873	486.7
		1.205			0.0790	0.0952		
0.8	1.205		428.5	2.6319			2.5921	390.9
		1.241			0.0788	0.0978		
0.7	1.276		357.4	2.5531			2.4943	312.1
		1.306			0.0773	0.1010		
0.6	1.336		299.1	2.4758			2.3933	247.3

This information may now be used to yield the value of x . To simplify notation, let $P_{(2\text{CO}+1\text{O}_2)} = P$ and $\frac{x i_{\text{CO}_2}}{i_{(2\text{CO}+1\text{O}_2)}} \cdot P_{\text{CO}_2} = P_c$. From a consideration of equation (3) we may say from

$$\frac{\left[\frac{\Delta \log (P + P_c)}{\Delta e^{-\lambda t}} \right]_{\text{catalyzed}}}{\left[\frac{\Delta \log (P + P_c)}{\Delta e^{-\lambda t}} \right]_{\text{normal}}} = 1$$

that for equal time intervals

$$\left[\frac{(P + P_c)_h}{(P + P_c)_h} \right]_{\text{catalyzed}} = \left[\frac{(P + P_c)_h}{(P + P_c)_h} \right]_{\text{normal}} \quad (5)$$

Applying equation (5) to the pressure in table 3, quadratic equations may be set up for several intervals and solved for x . These operations are summarized in table 4.

TABLE 4*
CALCULATION OF CATALYTIC EFFICIENCY (X) OF CARBON DIOXIDE

$e^{-\lambda t}$	EXPERIMENT 1			EXPERIMENT 2		
	$P_{(2CO+1O_2)}$	$1.48P_{CO_2}$	$P'_{(2CO+1O_2)}$	$P_{(2CO+1O_2)}$	$1.48P_{CO_2}$	$P'_{(2CO+1O_2)}$
1.0	629.7		629.7	629.7	620.1	$629.7 + 620.1x$
0.9	513.9	113.9	$513.9 + 113.9x$	486.7	760.7	$486.7 + 760.7x$
0.8	428.5	197.9	$428.5 + 197.9x$	390.0	855.0	$390.0 + 855.0x$
0.7	357.4	267.9	$357.4 + 267.9x$	312.1	932.5	$312.1 + 932.5x$
0.6	299.1	325.3	$299.1 + 325.3x$	247.3	996.3	$247.3 + 996.3x$

* Columns headed

$$P'_{(2CO+1O_2)} \text{ equal } P_{(2CO+1O_2)} + x \frac{i_{CO_2}}{i_{(2CO+1O_2)}} \cdot P_{CO_2}$$

$$\text{The ratio } \frac{i_{CO_2}}{i_{(2CO+1O_2)}} = \frac{1.52}{1.03} = 1.48.$$

Substituting values of $P' = (P + P_c)$ in equation (5) for the last three intervals⁷ in table 4, three values of x are obtained: 0.142, 0.144 and 0.148, which have an average value of 0.145 or 14.5%.

The constancy of the values of x are indicative of the validity of the above calculation. In subsequent calculations the average value of $x = 14.5\%$ will be used to find the true velocity of the alpha-ray reaction between carbon monoxide and oxygen. Though the value was determined for only a portion of the whole course of the reaction, it will be seen in a later section to hold for the whole.

The Recoil Atom Effect.—A study of the chemical effect of recoil atoms which was first discovered by Lind in the case of water synthesis⁸ has hitherto been confined to that reaction, in which it is particularly marked on account of the continued removal of the reaction product, water, from the gas phase. It therefore appeared to be of special interest to extend the study of the recoil-atom effect to a reaction where the product remains gaseous and can, therefore, exert a partial "screening" of the recoil atoms. Such a case is presented in the oxidation of carbon monoxide.

If we adopt the method of finding the pressure at which the combined action of alpha-rays and recoil atoms is just twice the rate due to alpha-rays alone, we may employ a modified form of the expression introduced by Lind⁹ $\frac{\alpha + R}{\alpha}$ in which α expresses the alpha-ray effect and R the recoil atom effect. By definition, they are equal to each other at the pressure sought, and at any other pressure, alpha varies directly with the pressure and may be placed equal to it at any pressure while R remains constant and equal to alpha at the point of equality. Therefore the expression $\frac{\alpha + R}{\alpha}$ is the abnormality factor which may be used to correct for the recoil atom effect.

In the present case we must substitute for alpha a new value α' which is really made up of the direct alpha-ray effect on the reactants plus that due to the action of alpha-particles on the inert gas carbon dioxide. The recoil atom effect R is that of recoil atoms on the pure reactant after correction has been made for the inert gas. Actually the alpha-ray effect in this case never drops to a point where it becomes equal to the recoil atom effect since it is sustained by the presence of the inert gas.

Table 5 contains the actual data and also the interpolated data in order to furnish more regular intervals. The column $P_{(2CO+1O_2)} = \alpha$ shows the course of the reaction with reference to the drop of partial pressure of the reactant; the column for α' gives the same corrected for the ionization contributed by the carbon dioxide; $\left(\frac{k\mu}{\lambda}\right)'_c$ is the velocity calculated from the values of alpha; $\left(\frac{k\mu}{\lambda}\right)'_{corr.}$ is calculated from the values of α' and therefore represents the velocity corrected for catalytic effect of inert gas. Neither of these approaches constancy.

The last column in which correction is made also for the recoil atom effect represents splendid constancy almost to the end of the reaction thus establishing the validity of the correction $\frac{\alpha' + R}{\alpha'}$, while the factor $\frac{\alpha + R}{\alpha}$ evidently is too large. By observing the values for $\left(\frac{k\mu}{\lambda}\right)'_{corr.}$ it will be seen that after correction for catalytic effect of carbon dioxide, they do exhibit a marked tendency to rise owing to the recoil atom effect, but never attain a value twice the original on account of the screening effect of carbon dioxide. Therefore, the actual value of R cannot be obtained from the data so directly as in the case of the water system and two methods for calculating R have been employed.

One method assumes inverse proportionality of R to diameter and specific ionization. The above-mentioned study of the water synthesis showed

TABLE 5

THE RECOIL ATOM EFFECT

EXPERIMENT 3. $2\text{CO}(\text{g}) + 1\text{O}_2(\text{g}) = 2\text{CO}_2(\text{g})$
 $D = 1.077 \text{ cm.}$ $E_0 = 33.79 \text{ mc. rn}$

ACTUAL DATA

$e^{-\lambda t}$	$P_{2\text{CO}+1\text{O}_2} = \alpha$	$P'_{2\text{CO}+1\text{O}_2} = \alpha'$	$\left(\frac{k\mu}{\lambda}\right)_c$	$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$	$\frac{\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}}{\frac{\alpha' + R}{\alpha'}}$
1.0000	689.3	689.3			
0.9698	602.1	614.6	132.6	112.4	102.6
0.9111	437.4	473.4	161.2	131.6	117.9
0.8803	371.9	417.3	155.9	121.2	106.3
0.8131	255.3	317.3	165.7	120.7	103.0
0.7828	209.9	278.4	191.3	127.8	105.7
0.7520	163.1	236.3	242.5	149.5	119.5
0.7158	117.8	199.5	266.1	145.3	113.1
0.6720	76.4	164.0	292.7	132.4	98.5
0.6281	35.3	128.8	520.6	163.3	114.3
0.5828	19.4	115.2	391.2	72.9	48.3
0.5277	13.1	109.8	210.9	25.8	16.6
0.3976	9.0	106.2	86.4	7.6	4.6
0.0000	0.0	99.1	163.6	5.2	3.2
				Average	106.0

INTERPOLATED DATA

$e^{-\lambda t}$	$P_{2\text{CO}+1\text{O}_2}$	$P'_{2\text{CO}+1\text{O}_2}$	$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$	$\frac{\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}}{\frac{\alpha + R}{\alpha}}$	$\frac{\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}}{\frac{\alpha' + R}{\alpha'}}$
1.00	689.3	689.3			
0.96	573.1	589.7	115.5	105.1	105.2
0.92	466.3	498.2	124.8	111.3	111.9
0.90	419.5	458.0	124.5	109.2	110.2
0.88	375.7	420.5	126.4	109.2	110.8
0.86	335.4	386.0	126.7	107.8	109.8
0.84	298.3	354.2	127.3	106.3	109.0
0.80	232.9	298.1	127.6	103.2	107.0
0.76	176.5	299.8	130.8	99.9	106.5
0.74	151.4	228.3	133.2	96.5	105.7
0.72	128.8	208.4	135.0	83.4	105.1
0.70	107.2	190.4	133.7	87.4	102.0
0.68	86.6	172.7	144.4	87.7	107.6
0.66	66.7	155.7	153.4	84.2	111.3
0.64	48.4	140.0	157.3	74.8	110.8

R equal to 118 mm. in a sphere of 0.9647 cm. diameter. For a sphere of 1.077 cm. diameter containing $2\text{CO} + 1\text{O}_2$ mixture, we should expect to find

$$R = \frac{118 \times 0.527 \times 0.9647}{1.03 \times 1.077} = 54.1 \text{ mm.}$$

where 0.527 and 1.03 are the specific ionizations of $2\text{H}_2 + 1\text{O}_2$ and $2\text{CO} + 1\text{O}_2$ mixtures, respectively. The second calculation anticipates a result to be presented later. It is found that the average velocity constant for the

first few intervals in a sphere of 1.848 cm. diameter was 37.0. If $\frac{\left(\frac{k\mu}{\lambda}\right)_{\text{corr.}}'}{\alpha' + R}$

is inversely proportional to the square of the diameter of the reaction vessel, as has been shown for the water synthesis, and if R is inversely proportional to the diameter, by using the velocity constant for the first measured interval of experiment 3, then

$$\frac{\frac{37.0 \times 1.848}{652.0 + \frac{1.077}{1.848} R}}{652.0} = \frac{\frac{112.4 \times 1.077}{652.0 + R}}{652.0}$$

from which we find R equals 61.9 mm. This is in excellent agreement with the preceding calculation when it is realized that as much as a ten per cent error in R will produce but a 1-2% error in the velocity constant in 1-cm. spheres, and a still smaller inaccuracy in larger vessels.

The Law of the Inverse Square of Diameters.—If chemical action in a gas or mixture of gases is proportional to the length of the mean path of the alpha particles within the volume, the velocity of reaction should increase linearly with the diameter of a sphere, other things being equal. But if the reaction is being measured by pressure change, as in the case with the present reaction, the pressure effect from a given amount of chemical action will diminish in inverse proportion to the volume or with the cube of the diameter. Combining these two effects predicts that the velocity constant measured in terms of pressure will diminish inversely with the square of the diameter.¹⁰

Since this relation has hitherto been tested only in the case of the synthesis of water, it appears desirable to test its validity for the oxidation of carbon monoxide. With this object in view, experiments were carried out of the same type already described except that no initial quantity of carbon dioxide was added. The results are contained in tables 6 and 7.**

Table 6 contains duplicate experiments in spheres of the same size in which it will be seen that the agreement between the mean velocity constants is satisfactory. Table 7 contains a similar experiment in a sphere of twice the diameter. It will be seen that the velocity constant now assumes a much lower value as one would expect.

TABLE 6

EXPERIMENT 4. $2\text{CO}(\text{g}) + 1\text{O}_2(\text{g}) = 2\text{CO}_2(\text{g})$
 $D = 1.844 \text{ CM. } E_0 = 31.81 \text{ MC. RN } R = 36.2 \text{ MM.}$

$e^{-\lambda}$	$P_{2\text{CO}+1\text{O}_2}$	$\left(\frac{k\mu}{\lambda}\right)'_c$	$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$	$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}} + \frac{\alpha' + R}{\alpha'}$
1.0000	671.4			
0.9274	599.1	49.3	42.0	39.7
0.8532	534.7	48.2	40.2	37.9
0.8152	508.5	41.6	34.1	32.0
0.7605	471.4	43.6	35.4	33.1
0.6830	420.7	46.2	36.9	34.3
0.6345	392.4	45.1	35.3	33.6
0.5875	365.4	44.0	34.0	31.3
0.5347	335.5	45.7	34.5	31.7
0.4753	311.4	47.4	35.1	32.0
0.4355	295.3	41.9	31.7	28.7
0.3348	252.3	49.1	34.9	31.4
0.2756	230.8	47.3	32.3	28.8
0.2321	214.0	54.6	36.3	32.2
0.1807	191.1	69.2	44.5	39.2
0.0000	114.4	89.3	50.8	43.7
			Average	35.6

EXPERIMENT 5. $2\text{CO}(\text{g}) + 1\text{O}_2(\text{g}) = 2\text{CO}_2(\text{g})$
 $D = 1.848 \text{ CM. } E_0 = 41.97 \text{ MC. RN } R = 36.1 \text{ MM.}$

$e^{-\lambda}$	$P_{2\text{CO}+1\text{O}_2}$	$\left(\frac{k\mu}{\lambda}\right)'_c$	$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$	$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}} + \frac{\alpha' + R'}{\alpha'}$
1.0000	848.5			
0.9418	731.6	60.7	51.5	49.2
0.6770	629.5	55.3	45.7	43.5
0.8395	563.4	48.3	36.5	34.5
0.7985	539.9	45.1	36.0	34.0
0.7606	499.0	49.5	38.9	36.5
0.7189	458.5	48.4	37.4	35.0
0.6762	421.3	47.2	35.6	33.2
0.6368	388.1	49.7	36.8	34.2
0.5945	357.8	45.8	33.2	30.7
0.5447	320.2	53.1	36.4	33.5
0.4941	283.4	57.5	39.1	35.7
0.4508	256.9	54.0	35.4	32.1
0.3931	221.9	60.5	38.0	34.2
0.2777	163.2	64.7	37.1	32.9
0.1982	127.4	72.4	36.4	31.7
0.1132	96.5	77.9	35.4	30.4
0.0658	82.1	81.3	31.5	26.6
0.0000	63.8	91.3	30.8	25.7
			Average	36.9

Table 8 contains a summary giving the average velocity constant in spheres differing by four-fold in diameter. The final column contains a constant corrected according to the Inverse Square of the Diameter Law which shows satisfactory agreement. The difference between the third and fourth

TABLE 7

EXPERIMENT 6. $2\text{CO}(\text{g}) + 1\text{O}_2(\text{g}) = 2\text{CO}_2(\text{g})$
 $D = 3.940 \text{ cm.}$ $E_0 = 67.0 \text{ cm. RN}$ $R = 16.1 \text{ mm.}$

$e^{-\lambda}$	$F_{2\text{CO}+1\text{O}_2}$	$\left(\frac{k\mu}{\lambda}\right)'_c$	$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$	$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}} + \frac{\alpha' + R}{\alpha'}$
1.0000	666.6			
0.9139	609.9	15.27	13.01	12.68
0.8673	582.7	14.45	12.17	11.84
0.8167	555.1	14.22	11.91	11.57
0.7577	527.2	12.92	10.72	10.40
0.6856	497.1	12.06	9.91	9.60
0.6188	469.3	12.74	10.35	10.02
0.5698	450.3	12.48	10.05	9.71
0.4868	421.9	11.61	9.23	8.91
0.4158	399.3	11.47	9.04	8.71
0.3474	378.1	11.79	9.19	8.84
0.1729	322.0	13.61	10.23	9.81
0.1035	301.0	14.37	10.59	10.11
0.0672	290.5	14.47	10.39	9.90
0.0202	277.5	14.38	10.39	9.90
0.0000	271.6	15.73	10.84	10.30
			Average	9.65

columns involves correction for differing average intensities of ionization (F) in different sized spheres. This correction is discussed by Glockler and Heisig¹¹ and is significant in large spheres.

TABLE 8

TEST OF THE INVERSE SQUARE LAW

D	$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}} \div \frac{\alpha' + R}{\alpha'}$	$\frac{\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}} \times D^2}{\frac{\alpha' + R}{\alpha'}}$	$\frac{\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}} \times D^2}{\frac{\alpha' + R}{\alpha'} \times F}$
1.077 cm.	106.0	123.0	123.0
1.844	35.6	121.1	120.0
1.848	36.9	126.0	124.1
3.936	9.65	149.0	136.8

Applying all of the corrections developed in this paper to the results of Lind and Bardwell,¹² i.e., the catalytic effect of carbon dioxide and the recoil atom effect, gives values for the velocity which have an average value the same as that of the present work for the same sized sphere, but which individually show a marked downward trend for which no explanation has been found.

Calculation of the M/N Ratio.—The method of calculating M/N ratio has been fully presented in several publications. We may state the result applied to the case, where M molecules of CO and O_2 are disappearing per N ion pairs produced in these gases by alpha particles, as:

$$-\frac{M_{(2\text{CO}+1\text{O}_2)}}{N_{(\text{CO}+\text{O}_2)}} = \frac{\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}} \cdot 2\lambda VA}{i \cdot F \cdot H \cdot 0.61D \cdot 11.16 \times 10^{10}}$$

where V and D are the volume and diameter of the spherical reaction vessel, A is Loschmidt's number, i is the specific molecular ionization of the stoichiometric reaction mixture, H is the correction factor for recoil atoms $\frac{\alpha' + R}{\alpha'}$, λ is the decay constant of radon, F is the average intensity of ionization and $\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$ is the velocity constant.

The quantity 11.16×10^{10} represents the total number of alpha particles emitted by radon in equilibrium through radium C , i.e., $3 \times 3.72 \times 10^{10}$, where 3.72×10^{10} is the number of alpha particles emitted each second per gram of radium.¹³ The quantity $0.61 \frac{D}{2}$ ($= 0.61 R$ where R is the radius) is the average path of an alpha particle.¹⁴ The values of i for carbon monoxide and oxygen are 100 and 110, respectively; hence, for the stoichiometric mixture $i = 1.03$. The form of the recoil correction has already been discussed. The value of A is 2.705×10^{19} cm.⁻³. For λ we shall use 2.099×10^{-6} sec.⁻¹.¹⁵ A series of F values for different pressures is taken from the recent calculations of the average number of ion pairs produced in air per centimeter of path per alpha particle, made by Glockler and Heisig¹⁶ using Mund's¹⁷ theoretical calculation of ionization produced by radon.

Grouping all terms constant throughout any given experiment, we have

$$\begin{aligned} -\frac{M_{(2\text{CO}+1\text{O}_2)}}{N_{(\text{CO}+\text{O}_2)}} &= \frac{\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}}{F \cdot H} \cdot \frac{2\lambda A V}{11.16 \times 10^{10} \cdot 0.61D \cdot i} \\ &= \frac{\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}}{F \cdot H} \cdot \frac{V}{D \cdot i} \times 1.668 \times 10^8. \end{aligned}$$

Table 9 contains a sample calculation of the M/N ratio for the carbon monoxide oxidation.

For experiments 3 and 5 the average values of the $-M/N$ ratio are 3.76 and 3.83. It is clear that the value of this ratio is between three and four in the carbon monoxide oxidation. It is of interest to note that a study of this reaction in a glow discharge produces a similar yield.¹⁸

Mechanism of the Carbon Dioxide Effect.—It has been quite difficult to find a wholly acceptable mechanism for any of the gas ion reactions. This difficulty is only enhanced in the case of the addition of an inert gas and its ions.

TABLE 9
 CALCULATION OF M/N RATIO FOR EXPERIMENT 4

$1.03P_{2\text{CO}+1\text{O}_2}$	F	H	$\left(\frac{k_{\mu}}{\lambda}\right)'_{\text{corr.}}$	$\frac{M_{(2\text{CO}+1\text{O})}}{N_{(\text{CO}+\text{O})}}$
691.5	2.83×10^4	1.054		
617.1	2.82	1.059	42.0	4.05
550.1	2.81	1.065	40.2	3.89
523.8	2.80	1.068	34.1	3.29
485.5	2.80	1.072	35.4	3.41
433.3	2.79	1.079	36.9	3.55
404.2	2.78	1.084	35.3	3.38
376.4	2.78	1.088	34.0	3.25
345.6	2.77	1.094	34.6	3.29
320.7	2.77	1.100	35.1	3.38
304.2	2.76	1.104	31.7	3.00
259.9	2.76	1.116	34.9	3.28
237.7	2.76	1.123	32.3	3.02
220.4	2.75	1.130	36.3	3.38
196.8	2.75	1.139	44.5	4.11
117.8	2.74	1.187	50.8	4.59
			Average	3.69

Two general types of mechanism have been proposed: (1) *Ion-clustering* in which it is assumed that the reactant molecules are brought together under the electrodynamic attraction of a central charge (positive and sometimes also negative ions) and that chemical reaction takes place upon neutralization of the charge by recombination of oppositely charged ions.

(2) *Dissociation of Ions*.—Either upon formation or neutralization of the ions, free atoms or radicals are formed which are chemically reactive.

The mechanism of the effect of an inert gas ion is fairly obvious for the first class if one assumes clustering about the foreign ion itself, which seems to present no electrodynamic difficulties. But in order for the foreign ion to exert an influence in the second type of mechanism, it is necessary to assume transfer of its energy by collision of the second kind, either during its life as an ion or immediately following its electrical neutralization, when the heat of ion recombination may be available.

The experimental evidence both in this reaction and in other reactions when CO_2 is present or produced indicates that CO_2 may have two oppositely directed effects. Its ions may tend to accelerate the ionic reaction, while its neutral molecules may have a retarding effect, which might be interpreted in the clustering mechanism as a "crowding out" or inefficiency effect due to CO_2 in the ion clusters. In the second hypothesis, the retarding effect of CO_2 molecules would be due to a "quenching" effect, that is, to an inefficient utilization of energy received by exchange. Too little is known of these effects to attempt at present to put them into the form of more definite mechanisms.

Summary.—The purpose of this paper was to ascertain the extent to which carbon dioxide influences the rate of the alpha-ray reaction in which it is produced by the union of oxygen and carbon dioxide. Only about 14.5% of the ionization falling upon CO₂ is found to be chemically effective.

The recoil atom effect on the oxidation of carbon monoxide was examined in a one-centimeter sphere. The correction to be applied to velocity con-

stants was $\frac{1}{\alpha' + R}$ where α' is the sum of the partial pressures of reactants

and the ionic equivalent pressure of the catalyst. The value of R found to be 62 mm. is in agreement with that predicted from the water synthesis.

The inverse square of the diameter law was shown to hold for this oxidation by comparing the values of $\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}} \div \frac{\alpha' + R}{\alpha'} \times D^2$ in spheres of several sizes. An average value of about 126 was obtained.

The M/N ratio for the reaction was calculated to be between three and four.

* Part of a Ph.D. Thesis submitted by Charles Rosenblum, University of Minnesota (1931).

** $\left(\frac{k\mu}{\lambda}\right)'_c$ is the velocity constant calculated on the basis of partial pressure of reactant, without correction for the ionic equivalent of carbon dioxide; $\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$ is the constant corrected for the fractional catalytic effect of the dioxide; $\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}} \div \frac{\alpha' + R}{\alpha'}$ is the latter constant corrected as described in the preceding section for the recoil atom effect.

¹ S. C. Lind and D. C. Bardwell, *J. A. C. S.*, **48**, 1575 (1926).

² S. C. Lind and D. C. Bardwell, *Ibid.*, **47**, 2686 (1925).

³ See footnote 1, p. 1582.

⁴ S. C. Lind and D. C. Bardwell, *J. A. C. S.*, **46**, 2005 (1924).

⁵ S. C. Lind, *J. A. C. S.*, **41**, 531 (1919).

⁶ S. C. Lind and D. C. Bardwell, *J. A. C. S.*, **48**, 1575 (1926).

⁷ In most alpha-ray reactions, the velocity is somewhat irregular at the start. Accordingly the value of x is not calculated for the first interval.

⁸ S. C. Lind, *J. A. C. S.*, **41**, 551 (1919).

⁹ *Loc. cit.*

¹⁰ S. C. Lind and D. C. Bardwell, *J. A. C. S.*, **46**, 2005 (1924).

¹¹ G. Glockler and G. B. Heisig, *J. Phys. Chem.*, **35**, 2478 (1931).

¹² S. C. Lind and D. C. Bardwell, *J. A. C. S.*, **47**, 2686 (1925).

¹³ Hess and Lawson, *Wien. Ber.*, **127**, 405 (1918).

¹⁴ S. C. Lind and D. C. Bardwell, *J. A. C. S.*, **45**, 2585 (1923).

¹⁵ Curie and Chamie, *J. de Physique et Radium*, **5** [6], 238 (1924).

¹⁶ See footnote 11.

¹⁷ Mund, *J. Phys. Chem.*, **30**, 890 (1926).

¹⁸ Brewer and Kueck, *Ibid.*, **35**, 1281 (1931).