hydes reacted vigorously. The solubility of sulfur was determined quantitatively for temperatures between 0° and 65°.

AMES, IOWA

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE CHEMICAL ACTION OF GASEOUS IONS PRODUCED BY ALPHA PARTICLES.[1] VI.[2] REACTIONS OF THE OXIDES OF CARBON

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In 1912 one of us collected the data[3] on chemical reaction under the influence of α-radiation and found close equivalence between the number of molecules (M) reacting chemically and the number of ions (N). Although the data were not sufficiently accurate to establish exact reaction mechanisms, it was sought to generalize the principle discovered into a modified form of Faraday's law applying to gaseous ions,[4] while still recognizing that, owing to the variety of the latter, the gaseous-ionic would not necessarily be identical with the electrolytic equivalents. This principle of equivalence was questioned by Debierne[5] and Wourtzel[6] on account of their experiments showing that *two* or *three* molecules of hydrogen sulfide, nitrous oxide or ammonia gas are decomposed for each ion pair instead of only *one* molecule of each.

If it were true that each molecule ionized by an α-particle decomposed directly, then $-M/N = 1$ would be expected. The results, however, of later work by the writers, including the present and subsequent papers, show that the first step is one of addition of neutral molecules to the ions and not of decomposition of the latter. Even when decomposition is the final result, it takes place through intermediate formation of an ion-addition product. There are, then, at least two processes by which the M/N ratio is multiplied a few fold beyond unity. Consequently, the values of $M/N > 1$, instead of disproving the *ionic* nature of the reaction,

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[1] Published with permission of the Director of the Bureau of Mines.

[2] The five preceding papers [THIS JOURNAL, **41**, 531, 551 (1919); **45**, 2585, 2593 (1923); **46**, 2003 (1924)], which will be referred to as Part I, Part II, etc., were published under the general title "Chemical Action Produced by Radon." The series is now continued under a changed title to lay stress on *ionization* as a mode of chemical activation, rather than on radon as the agency which happens to afford the most convenient means of obtaining ionization in known quantity.

[3] Lind, *J. Phys. Chem.*, **16**, 564 (1912).

[4] Lind, *Le Radium*, **9**, 426 (1912); *Z. physik. Chem.*, **84**, 759 (1913).

[5] Debierne, *Ann. phys.*, [9] **2**, 97 (1914).

[6] Wourtzel, *Compt. rend.*, **157**, 929 (1913); *Le Radium*, **11**, 289, 332 (1919); *J. Phys. Rad.*, **1**, 77 (1920); **2**, 53 (1921).

greatly support it. The laws which have been found to govern these multiplying effects also accord with other recently established physical properties of gas ions. The two multiplying processes are: (1) clustering, by which the primary ion collects one or a few other neutral molecules and carries them into the chemical reaction with it and (2) the attachment of the primary free electron to a neutral molecule, forming a negative ion which thus becomes equal in chemical activity to the positive ion, and also forms clusters.

The steps of the general mechanism are as follows. Assume a binary compound A_xB_y. Ionization by an α-particle consists in the removal of only *one* electron[7] as

$$A_xB_y + [\alpha] = (A_xB_y)^+ + (-) \qquad (1)$$

When a molecular ion like $(A_xB_y)^+$ is produced by α-particles, we have no direct physical evidence as to what happens to it—whether it dissociates or not. The indirect evidence which we have adduced in many cases of chemical reaction indicates that it *does not dissociate* before losing its charge, and we make that general assumption.

The positive ion then combines with one or more neutral molecules either of its own or of a different kind; when of its own kind the resulting cluster frequently embraces only two, but sometimes several, molecules, as

$$(A_xB_y)^+ + A_xB_y = (A_xB_y)_2^+ \qquad (2)$$

There is recent physical evidence, both theoretical[8] and experimental[9,10] for this step, which also finds a parallel in some photochemical reactions[11] having a ratio $M/h\nu = 2$.

The next step depends on what becomes of the liberated electron. When no gas is present with affinity for free electrons[12] their only function is to reëstablish electrical neutrality by combining with the clustered positive ions as

$$(A_xB_y)_n^+ + (-) = (A_xB_y)_n \qquad (3)$$

When, however, a gas like oxygen is present which has a great affinity for free electrons,[12a] they will be trapped by O_2 to form O_2^- before recombining with the parent positive ion,

$$O_2 + (-) = O_2^- \qquad (4)$$

followed by clustering with their own or other molecules

$$O_2^- + nO_2 = (O_2)^-_{n+1} \qquad (5)$$

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[7] Millikan and Fletcher, *Phil. Mag.*, [6] **21**, 753 (1911). Millikan, Gottschalk and Kelly, *Phys. Rev.*, [2] **15**, 157 (1920).

[8] Thomson, *Phil. Mag.*, **47**, 337 (1924).

[9] Erikson, *Phys. Rev.*, [2] **17**, 400 (1920); **20**, 117 (1922).

[10] Wahlin, *ibid.*, **20**, 267 (1922).

[11] Bonhoeffer, *Z. Physik*, **13**, 101 (1923). Bowen, *J. Chem. Soc.*, **123**, 2328 (1923). Warburg, *Z. Elektrochem.*, **26**, 54 (1920). Bodenstein and Kistiakowski, *Z. physik. Chem.*, **116**, 371 (1925).

[12] (a) Loeb, *Phil. Mag.*, [6] **43**, 229 (1922). (b) Lind, *Trans. Am. Electrochem. Soc.*, **44**, 66 (1923).

Exclusive Oxidation.—The affinity of oxygen for free electrons produces a very important effect by which oxidation replaces all other reactions that would occur in its absence. It depends on the general assumption (to be supported by much experimental evidence) that *final chemical action does not result until electrical neutralization is brought about by recombination of the positive and negative ions or clusters.*[13] When there are no free electrons but all are trapped[14] by O_2 to form O_2^- ions, *oxidation will be a necessary consequence and will constitute the exclusive reaction,* provided the positive ion consists of oxidizable material. This will be shown for carbon monoxide and in later papers for methane, ethane, cyanogen, acetylene, etc., meaning that ionization produces in these gases, when alone, certain reactions of decomposition or polymerization, as the case may be, but when oxygen is present, they do not even in part undergo their own reactions, but are selectively oxidized, as

$$(A_xB_y)^+ + (O_2)_n^- = A_xB_yO_{2n} \left[\begin{array}{ll} \rightarrow (1) & A_xB_yO_{2n} \\ \text{or} & \\ \rightarrow (2) & A_xO_{n_1} + B_yO_{n_2} \\ \text{or} & \\ \rightarrow (3) & A_xO_{2n} + B_y \end{array}\right. \qquad (6)$$

and no reaction of Type 3.

In general, whether oxygen is present or not, ionic cluster or complex formation is the first step in ionic reactions. When the clusters are electrically neutralized, the combined cluster may undergo one or more of the following processes: (1) stabilization of the di- or polymeric addition product, or (2) decomposition of the complex (a) to original state, (b) to simpler compounds or (c) to the elements.

Any simultaneous combinations of (1) or (2) will be possible through simultaneous reactions.

The great frequency of the formation of stable addition products which we find under all ionizing conditions, demonstrates to our satisfaction the reality of ion clustering, a matter about which physicists have entertained variant views. A cluster theory of ionic chemical reaction was earlier proposed by Lind[15] for ozonization of oxygen by α-particles, but owing to the view then prevalent among physicists that ionic mobility in electrical fields indicated absence of clustering, the theory was not fully ac-

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[13] This may be regarded as contradicting the earlier statement of principle by Lind[12b] that ions (and other activated molecules) do not interact with each other but rather with neutral or unactivated molecules. It is not a contradiction but rather an extension or modification. Addition of ions to neutral molecules comes first, forming ion clusters of sufficient stability to hold together until combination of + and − clusters takes place, resulting in the formation of the final stable chemical compounds. (See also Discussion.)

[14] This is possible owing to the high concentration of oxygen molecules relative to the low (momentary) concentration of + ions, which also are in competition for free electrons.

[15] Lind, *Am. Chem. J.*, **47,** 414 (1912).

cepted. Loeb[16] has recently shown that little or no conclusion can be drawn from ionic mobility as to ionic mass or clustering. It appears therefore that the chemical evidence for clustering is now more definite than the physical, although some degree of clustering has been shown by Erikson,[9] Wahlin[10] and their co-workers in a few of the simpler gases.

Previous Experiments

The preceding papers (Parts I to V) have been confined to the reaction, $2H_2 + O_2 \longrightarrow (2H_2O)$. On account of its simplicity this reaction was employed to establish the general laws for reaction brought about in gases by radon.

Briefly, the following are the principles established. In a small container (with no dimension exceeding a few centimeters, the range of the shortest α-rays) filled with electrolytic gas and radon, the velocity of reaction is proportional to the quantity (not to the concentration) of radon, which supplies the radiation, and to the gas pressure, which determines the portion of radiation rendered effective by its absorption. Thus, the length of average path of the α-particles in the gas controls the reaction velocity. For convenience of calculating the average path[17] spherical vessels are used. On increasing the size of the sphere the reaction produced by a given quantity of radon is increased in proportion to the diameter, since the average path of α-particles is lengthened linearly. (This increase results in spite of the diminished concentration of radon.)

Varying the proportions of hydrogen and oxygen produces a change in reaction velocity which has *no relation to mass action* but depends directly on the change in specific ionization; excess of hydrogen diminishes, while excess of oxygen enhances the rate. This indicates that total ionization of both oxygen and hydrogen is the primary cause of reaction which is supported by the absolute value of the M/N ratio. Our present view of the mechanism, which is a modification of the one given in Part I, is as follows.

$$O_2 + [\alpha] = O_2^+ + (-);\ O_2^+ + 2H_2 = (H_2O_2H_2)^+ \text{ (gas-ion cluster)}$$
$$O_2 + (-) = O_2^-;\ O_2^- + 2H_2 = (H_2O_2H_2)^- \text{ (gas-ion cluster)}$$
$$\text{upon combination of } + \text{ and } - \text{ clusters: } H_8O_4 = 4H_2O.$$

Similarly, for hydrogen.

$$H_2 + [\alpha] = H_2^+ + (-);\ H_2^+ + O_2 + H_2 = (H_2O_2H_2)^+$$
$$O_2 \text{ (never } H_2) + (-) = O_2^-;\ O_2^- + 2H_2 = (H_2O_2H_2)^-$$

Upon combination: $H_8O_4 = 4H_2O$. In either case, 4 molecules of water result from 1 original ion pair, which agrees with the value found experimentally, $M_{H_2O}/N_{(H_2 + O_2)} = 4$.

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[16] Loeb, *Phil. Mag.*, [6] **48**, 446 (1924). Loeb and Ashley, *Proc. Nat. Acad. Sci.*, **10**, 351 (1924).

[17] Lind, American Chemical Society Monograph No. 2, Chemical Catalog Co., New York, **1921**, p. 82.

The same general principles apply to other gas reactions and we have used the same methods with slight modification in studying them. Two procedures are applicable: (1) mixing radon directly in the reacting gases (Part I); and (2) confining radon in a thin, minute α-ray bulb (Parts III and IV) at the center of a sphere containing the reactants. In some cases Procedure 2 cannot be used when liquid or solid products are formed, if they deposit on the α-ray bulb, making it too thick to transmit α-rays.

The data which are used to establish a reaction mechanism are the following. (1) The reaction-velocity constant, obtained by applying a kinetic equation to the manometric course of the reaction, (Part I, p. 536). In some cases a knowledge of the pressure change at ordinary temperature does not suffice and measurement at lower temperature to eliminate some of the components is required. We were fortunate in having advantage of the precise platinum resistance thermometry of the Cryogenic Laboratory of the Bureau of Mines, which is regarded as accurate to 0.01–0.02° down to liquid-air temperatures. (2) Determination of the M/N ratio and observation of its change, if any, as the reaction proceeds. (3) Chemical analysis of the end-products of reaction. Owing to the small quantities with which we are dealing, the final analysis is limited to the gaseous products. When solids or liquids are formed, special methods must later be developed for accumulating them in quantity sufficient for identification and analysis.

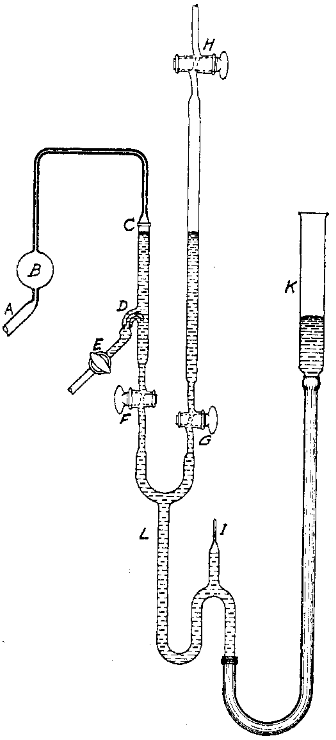

Fig. 1.

Present Procedure.—The apparatus shown in Fig. 1 is attached to the radon collecting system at A and to the high vacuum line through H. With the stopcock E closed and the mercury level at I, the whole system is evacuated to 0.0001 mm. pressure. The mercury level is then raised to the capillary just above C, filling the system CDEF. The stopcock F is closed and the mercury level raised through the stopcock H, which is then closed. The tube between H and G is of the same bore as the tube leading to C, and is used as a closed manometer for measuring small pressures in the Bulb B. Radon, purified by the chemical method previously described,[18] is introduced into Bulb B and the capillary between A and B sealed off. The residual pressure of the radon and impurities measured by the closed manometer never exceeded 0.2 mm. The gas to be radiated is introduced four hours after the radon is in place. A Ramsay buret (see Fig. 2) containing the gas is connected at E and all connecting tubes are evacuated.

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[18] Ref. 15, p. 406.

The mercury level is lowered by opening F below the mouth of the insealed tube at D. The stopcock E is then opened and the gas from the buret introduced. Without the insealed tube at D, a spray of mercury is often found in the bulb B after introduction of the gas to be radiated. This is avoided when the mercury between E and D is directed downward by the curved insealed tube. Immediately after the gas is introduced its pressure is measured, the mercury being set at the lower edge of the band at C, with the bulb B immersed in a thermostat at 25°. After the reading is taken the mercury level is raised just into the capillary tube (0.2mm. bore) leading to the bulb and the stopcock F closed. The observed pressure is multiplied by a factor correcting for the volume between the marker C and the capillary. Pressures near atmospheric were measured with the open manometer K, and the barometric pressure was added. Temperatures below 0.0° were measured with a platinum-resistance thermometer, accurate to 0.01° down to —190°.

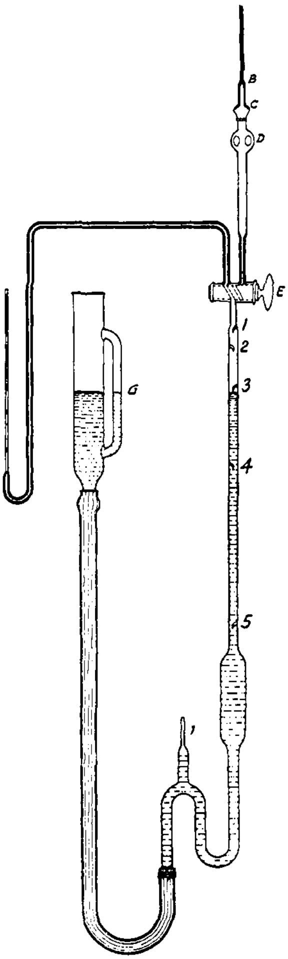

Fig. 2.

Preparation of Gases.—Carbon dioxide was prepared by dropping dil. hydrochloric acid on potassium carbonate. The gas was bubbled through a solution of potassium acid carbonate and dried by passing through a phosphorus pentoxide tower. It was found to be over 99.9% pure by absorption in alkali.

Carbon monoxide was prepared by dropping concd. sulfuric acid on c. p. formic acid. It was dried by bubbling through concd. sulfuric acid and passing through a phosphorus pentoxide tower. It contained no oxygen and was found to be 99.9% pure by absorption in ammoniacal cuprous chloride solution.

Oxygen was prepared by heating potassium permanganate in a system previously evacuated. The gas was liquefied and fractionated, the middle fraction being taken as pure. Foreign gas not absorbed by phosphorus or by pyrogallol solution did not exceed 0.1%.

Hydrogen was generated electrolytically from a 20% solution of potassium hydroxide, using nickel electrodes. The gas was passed through a tower of platinized asbestos heated to 400° and dried with phosphorus pentoxide. Over 99.9% was found to pass through a palladium thimble to be described later.

Analysis of Gases.—Gases were always dried in eudiometer tubes over mercury before being measured. The gas to be measured was taken into a gas buret (see Fig. 2) through a capillary "goose neck."[19] The mercury meniscus in the buret (Fig. 2) was set at that glass marker giving the nearest to atmospheric pressure; the manometer column leading to an open manometer was measured with a cathetometer that had been calibrated against a standard meter bar. Barometric pressure was read and added algebraically to the manometer column. The temperature of the gas in the buret was taken as that of a mercury thermometer adjacent to it. Fluctuations in room temperature were found to be slight during the time of measurement.

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[19] Cameron and Ramsay, *J. Chem. Soc.*, **93**, 966 (1908).

Analysis of mixtures was made in the following order: carbon dioxide, oxygen, hydrogen and carbon monoxide.

For absorption of carbon dioxide, a piece of stick potassium hydroxide about the size of a pea was fused in the closed end of a eudiometer tube of 4mm. bore and 110 mm. length until it formed a smooth layer. After being cooled, the tube was completely filled with mercury and inverted in a mercury trough. The gas to be tested was introduced from the gas buret. At room temperature the absorption of carbon dioxide by dry potassium hydroxide is extremely slow. It was found, however, that heating the alkali externally to incipient fusion resulted in immediate absorption of carbon dioxide. When cooled, the potassium hydroxide took up any moisture given off during heating and the gas was again dry. This procedure was found to give reproducible results and was satifsactory in every way.

To test for oxygen, the gas was introduced into a eudiometer tube containing alkaline pyrogallol solution. After the tube had been shaken until no further absorption took place, the gas was transferred to a eudiometer tube containing potassium hydroxide and dried before it was measured in the gas buret.

Hydrogen was removed by a palladium thimble. The palladium thimble (50 mm. long, 3 mm. in bore and of 0.3mm. wall thickness) (Fig. 2, AB) was gold-soldered to a platinum funnel BC at B. The platinum funnel was in turn joined by lead glass to the bulb D at C. Several small pieces of potassium hydroxide were fused to the inner wall of the bulb to insure dryness in the system. The system above the stopcock E was evacuated, using the buret as a pump. The palladium thimble was heated by a small resistance furnace to 200–225°, at which temperature hydrogen diffuses through very rapidly. Care must be taken not to allow liquid mercury to enter the thimble, as it seems to poison the surface. After the thimble had been evacuated, the gas to be tested was introduced and the thimble kept at 200–225° until no further contraction resulted. When small quantities (1 cc.) of gas were tested, the absorption was complete in one hour. With larger quantities of gas, the diffusion was allowed to continue overnight. After completion of the process, the residual gas was pumped into a eudiometer tube and then taken into the buret and measured.

Carbon monoxide was absorbed by fresh ammoniacal cuprous chloride solution in a eudiometer tube.

Calculation of M/N Ratios.—The velocity constant $K\mu/\lambda$ is evaluated by integration of the differential equation $\mathrm{d}P/\mathrm{d}t = kPE$.[20] If P is in mm. of mercury and t in seconds, the number of molecules, M, reacting per second is: $M = (\mathrm{d}P/\mathrm{d}t)(v/760) \times A = -(k\mu/\lambda)\lambda EP(v/760)A$, where A is the number of molecules per cc. (N. T. P.), or 2.705×10^{19}; λ is 2.085×10^{-6} sec.$^{-1}$ for radon; V is volume in cc.; and E is radon in curies. The number of ions produced in the bulb per second is $N = B \times C \times F \times G \times H \times (P/760) \times E$, where B is the number of α-particles per second from 1 curie of radon in equilibrium with Ra D taken as[21] 11.16×10^{10}; C is the average path, 0.305 D (Part III), where D is diameter in centimeters; F is the average intensity of ionization (Part III) calculated on 2.37×10^{5} ions[22] in the completed path of an α-particle from Ra C′; G is Bragg's (ks) specific molecular ionization; and $H = \alpha +$

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[20] Ref. 17, p. 96.

[21] Hess and Lawson, *Sitzb. Akad. Wien*, **127**, 405 (1918); *Z. Physik*, **24**, 402 (1924).

[22] Geiger, *Proc. Roy. Soc.*, **82**, 486 (1909).

R/α, where α and R are α-ray and recoil-atom effects, respectively (Part V). Substituting, we have $\frac{M}{N} = \frac{(k\mu/\lambda)\ V}{DFGH} \times 1.66 \times 10^3$. Lower values for the number of α-particles per second from 1 g. of radium and the number of ions per α-particle in its completed path would lead to correspondingly higher values for the M/N ratio.

Decomposition, Oxidation and Reduction of the Oxides of Carbon

3. **Decomposition of Carbon Monoxide.**—Cameron and Ramsay[23] first studied the decomposition of carbon monoxide by radon using 25 milli curies in a volume of about 2.5 cc. The total pressure diminished from 299.2 to 249.7 mm. and the residual gas they found to consist of: 0.084 cc. of carbon dioxide, 0.041 cc. of oxygen and 0.755 cc. of carbon monoxide, indicating that "the monoxide decomposed to form carbon and both *oxygen* and carbon dioxide, although it is possible that the carbon dioxide was produced by the interaction of the oxygen and carbon." The results of Cameron and Ramsay were used by one of us[24] to study the kinetics of the reaction and also to determine the ratio $-M_{CO}/N_{CO}$ (number of molecules of carbon monoxide decomposed per ion pair), which was found to be 1.86.

We have measured the reaction a number of times under different conditions. The data of a typical experiment are shown in Table I. In no case have we been able to find any free oxygen present, although the carbon dioxide formed is never sufficient to account for the whole diminution in pressure, assuming the reaction $2CO = CO_2 + (C)$. This suggested that possibly oxygen once free or nascent had reacted with the mercury of the manometer system. An experiment carried out in the complete absence of mercury failed to confirm this; again no free oxygen was found, but still the decrease of pressure was greater than would correspond to the carbon dioxide formed.

We then thought for a time that the deficiency of carbon dioxide could be accounted for by adsorption of carbon dioxide by the free carbon. This view has been shaken by two observations. (1) The ratio of the number of molecules of carbon monoxide decomposed to the number of molecules of carbon dioxide formed is about 3 throughout the entire course of the reaction.[25] This would hardly be expected if a changing mixture of carbon dioxide and carbon monoxide were being adsorbed in an increasing quantity of carbon. (2) From time to time a brownish-red color was observed through the glass walls of the reaction spheres.

Sub-oxide of Carbon.—Owing to the blue or brown color ordinarily

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[23] Cameron and Ramsay, *J. Chem. Soc.*, **93**, 982 (1908).

[24] Lind, Ref. 3, p. 589; "Chemical Effects of Alpha Particles," Chem. Catalog Co., New York, **1921**, pp. 85, 97.

[25] The value should, of course, be 2 were it not for the influence under discussion.

produced in the glass itself by the rays, the other colored material escaped conclusive observation until reaction bulbs were broken open so that the inner surfaces could be seen directly and examined under the microscope. Besides free carbon which partly collected in a loose, fluffy condition at the bottom of the vessel and some isolated masses of carbon irregularly deposited over the walls, there was also a yellow-brownish film quite evenly deposited over the inner surface. The film, about 0.5μ thick, has properties similar to those of a collodion film. It clings to the wall rather tenaciously, can be ruptured by scratching, is sometimes found rolled back, leaving a bare surface of glass, and can be detached in coherent films by immersion in water. It has revealed no outstanding chemical properties, remains undissolved in water, acid or alkali solution, slowly disappears in concd. nitric acid, as if being oxidized and disappears slowly in concd. potassium hydroxide solution, but does not dissolve in any of the common organic solvents. Before it can be analyzed it will have to be obtained in greater quantity and separated from the free carbon. This will be reported upon later.

The color of the film, together with the circumstances of its formation, suggests a *sub-oxide of carbon.* Berthelot[26] described a sub-oxide (C_4O_3) which he obtained by the action of silent electric discharge ("l'effluve") in carbon monoxide gas, but its properties do not describe what we have. Brodie[27] claimed that a series of sub-oxides, C_2O, C_3O_2, C_4O_3, C_5O_4, are formed from carbon monoxide in the induction tube. Donath and Burian[28] have recently reviewed the sub-oxides of carbon and Ott[29] has presented new results on the effect of glow discharge on carbon monoxide, including the formation of a sub-oxide (C_3O_2).

As already stated, it is not the object of the present paper to determine all of the solid products of the reactions dealt with, but rather to find the ratio of ionization in the gas to chemical change in the gaseous constituents. The sub-oxide formation from carbon monoxide is a complication of the reaction which will be dealt with later in a separate paper. Our present knowledge would indicate a reaction such as $6CO = 2CO_2 + (C) + (C_3O_2)$; and $x(C_3O_2) = (C_3O_2)_x$, solid sub-oxide film. This formulation conforms with the factor $3CO:1CO_2$ but cannot be brought into direct agreement with the $-M_{CO}/N_{CO}$ ratio of 2, which is readily compatible with the simple mechanism already proposed by one of us,[12b] $CO^+ + CO = (CO)_2^+$ and $(CO)_2^+ + (-) = CO_2 + (C)$. The dilemma of finding polymers higher than predicted by the M/N ratio is sufficiently general to merit attention. One assumption which is difficult to test is that some complexes have a

[26] Berthelot, *Compt. rend.*, **82**, 1360 (1876).

[27] Brodie, *Proc. Roy. Soc.*, **21**, 245 (1873).

[28] Donath and Burian, *Ahrens Samml. Chem. Vorträge*, **27**, 469 (1924).

[29] Ott, *Ber.*, **58**, 772 (1925).

fairly long life after electrical neutralization, giving them time to meet other clusters and form, without further ionic intervention, still higher polymers, which would eventually break down into the final products or else be stabilized. For carbon monoxide this would give the following series of events: $(CO)_2^+ + (-) = C_2O_2$; $3nC_2O_2 = (C_2O_2)_{3n}$; $(C_2O_2)_{3n} = 2nCO_2 + n(C) + (C_3O_2)_n$.

A plausible suggestion by Professor Franz Fischer is that a product formed in the gas phase polymerizes at the walls. This would account for the uniform thickness of the film. However, the fact that free carbon largely falls by gravity into the bottom of the vessel indicates that the first change in the complex occurs in the gas phase, since the film of $(C_3O_2)_n$ seems to hold tenaciously any carbon that comes in contact with it.

Ott[29] formulates the reaction in *glow discharge* as $4CO = C_3O_2 + CO_2$. His evidence for a 1:1 relation of C_3O_2:CO_2 is quite satisfactory, but his failure to observe any free carbon is puzzling, and his ratio of 4CO:1CO_2 appears to rest on less conclusive evidence than our 3CO:2CO_2. Of course, the reaction under glow discharge may not be identical with that under α-radiation, but the sub-oxides obtained have strikingly similar properties in the two cases.

Data for the decomposition of carbon monoxide are shown in Table I.

TABLE I

DECOMPOSITION OF CARBON MONOXIDE

Approximate reaction: $6CO \longrightarrow 2CO_2 + (C) + (C_3O_2)$

Bulb: vol., 4.071 cc.; diam., 1.981 cm. $E_0 = 0.1023$ curie

Time Days	Hours	$P_{(total)}$	P_{CO}	$(K\mu/\lambda)'$	$-P_{CO}/P_{CO_2}$	$-M_{CO}/N_{CO}$
0	0	698.6	689.6			
0	11.0	635.9				
0	11.17	(635.2)	610.9	14.8	3.24	1.85
0	23.42	591.4				
0	23.75	(590.4)	544.1	13.7	3.04	1.71
1	4.17	577.2				
2	0.25	532.0				
2	6.5	(530.5)	452.7	12.8	2.90	1.6
2	23.7	494.8				
3	0.83	(494.1)	403.9	9.53	3.93	1.19
3	23.3	469.7				
4	1.67	(468.2)	365.9	9.82	3.14	1.23
6	0 0	438.6				
6	0.17	(438.4)	322.8	8.66	3.24	1.08
8	2.67	418.8				
8	2.83	(418.7)	291.8	9.21	2.74	1.15
10	0.0	(410.1)	277.7	6.74	2.56	.84
17	4.5	(393.0)	248.4	9.59	2.40	1.20
∞		386.4	239.9		4.50	

Over total reaction $\dfrac{P_{CO}}{P_{CO_2}} \begin{cases} = 3.07 \text{ from room temperature and liquid-air measurements} \\ = 3.08 \text{ from gas analysis at end.} \end{cases}$

TABLE I (*Concluded*)

ANALYSIS

Cc. (N. T. P.)	Total vol.	CO	CO_2	O_2
Initial	3.694	3.694	0	0
Final	2.070	1.285	0.785	0

BALANCE SHEET OF ELEMENTS

(For convenience we treat atoms in units of their volumes as gases.)

	C	O
Initial	3.694	3.694
In gas phase at end	2.070	2.855
As solids at end	1.624	0.839

Therefore the empirical formula of total solid (which is a mixture of components) is $C_{1.94}O$, or approximately $(C_2O)_x$. When this solid is heated to 400° the oxygen is completely liberated as a mixture 75% carbon dioxide and 25% carbon monoxide by volume, leaving about 70% of the carbon free.

The pressures in Col. 3 are the total pressures measured at room temperature and reduced to 0°. The pressures in parentheses are interpolated to correspond to the times for the pressures of carbon monoxide given in Col. 4. The pressures of carbon monoxide given in Col. 4 were measured in liquid air and reduced to 0°. The velocity constant $(k\mu/\lambda)'$ given in Col. 5 is calculated "step-wise" on the measured partial pressure of carbon monoxide. Col. 6 gives the ratio of carbon monoxide disappearing to carbon dioxide formed, also calculated "step-wise." The last column gives the ratio of the molecules of carbon monoxide disappearing per pair of ions produced from carbon monoxide. It shows a trend downward. An experiment in which carbon dioxide was radiated in a bulb containing the deposit from carbon monoxide decomposition showed that carbon dioxide ions oxidize the deposit, giving back carbon monoxide. This back reaction is responsible, at least in part, for the drop in M/N ratios and velocity constants.

The final analysis and balance sheet given at the end of Table I are conclusive proof that oxygen is in some way retained in the solid deposit.

In addition to experiments carried out by mixing radon with carbon monoxide, the latter was radiated by radon confined in an α-ray bulb at the center of a reaction sphere (compare Part III), provided with a side arm for condensing carbon dioxide in liquid air. Initially $-(M_{CO}/N_{CO})$ has the value 2.35 which drops to 1.51 after 12 hours. The α-ray bulb became coated with black deposit. The results are therefore of uncertain accuracy but point to a value for $-(M_{CO}/N_{CO})$ about the same as those obtained in mixtures.

Oxidation of Carbon Monoxide by Oxygen

The oxidation of carbon monoxide is a very simple, straightforward reaction, which confirms and illustrates the principles already cited. Ionically the reaction may be expressed as follows.

$$CO + [\alpha] = CO^+ + (-);\ CO^+ + CO + O_2 = (CO.O_2.CO)^+$$
$$CO + (-) \longrightarrow \text{no affinity; but } O_2 + (-) = O_2^-;\ O_2^- + 2CO = (CO.O_2.CO)^-$$

or from each ion pair: $4CO + 2O_2 \longrightarrow 4CO_2$. The M/N ratios found experimentally are shown in Tables II, III, IV and V. The case is seen to be exactly parallel to that of formation of water, substituting carbon monoxide for hydrogen throughout. The + cluster is also formed from O_2^+.

Analysis shows that carbon dioxide accounts for 99% of the carbon monoxide disappearing.

The ratio $M_{(CO + O_2)}/N_{(CO + O_2)}$ is not as constant throughout the reaction as was found by Lind to be the case for electrolytic gas. However, this case is different in that the carbon dioxide formed remains in the gas phase and is, of course, ionized. The possible effect of carbon dioxide slightly reducing the efficiency of carbon monoxide oxidation cannot be treated quantitatively until more data are obtained in similar cases.

TABLE II

Reaction: $2CO + O_2 = 2CO_2$. (Stoichiometric mixture)
Bulb: vol., 5.274 cc.; diam., 2.160 cm. E_0 = 0.0663 curie

Time Days	Time Hours	$P_{(\text{total})}$	$P_{(2CO + O_2)}$	CO_2	$(K\mu/\lambda)'$	$\frac{-M_{(CO + O_2)}}{N_{(CO + O_2)}}$	Radon, % remaining
0	0	845.3	845.3	0.0			100.00
0	7	795.2	696.3	98.9	57.2	8.38	94.88
0	16.5	752.5	569.9	182.6	46.3	6.78	88.36
0	20.0	740.3	533.8	206.5	43.3	6.35	86.07
1	0.0	728.5	498.9	229.6	40.1	5.88	83.53
1	5.5	713.4	454.6	258.8	41.6	6.10	80.15
1	6.0	(451.3)	451.3	($CO + O_2$) measured in liq. air			79.85
1	17.0	688.7	382.1	306.6	39.5	5.78	73.53
2	6.5	668.4	322.9	345.5	36.0	5.27	66.45
2	17.0	656.2	287.7	368.5	34.6	5.06	61.42
3	17.0	634.2	224.0	410.2	37.4	5.38	51.30
3	18.5	(223.0)	223.0	($CO + O_2$) measured in liq. air			50.73
5	17.0	607.5	147.6	459.9	40.6	5.95	35.79
7	0.0	597.4	119.1	478.3	43.6	6.39	28.36
∞		569.4	43.8	525.6	53.2	7.80	0.0
			Over the entire period:		44.6	*6.54*	
				Theory		**6.00**	

ANALYSIS

Cc. (N. T. P.)	Total	CO	O_2	CO_2
Initial	5.866	3.911	1.955	0.00
Final	3.953	0.220	0.084	3.649
Reacted		3.691	1.871	
Correcting for gas law				
3.649 CO_2 would form from		3.674	1.837	
Unaccounted for		0.017	0.034	

TABLE III

Reaction: $2CO + O_2 = 2CO_2$. Initially $1CO$ to $1O_2$

Bulb: vol., 5.196 cc.; diam., 2.149 cm. $E_0 = 0.0584$ curie

Time						$(K\mu/\lambda)'$ Calcd. on	
Days	Hours	$P_{(\text{total})}$	P_{CO}	P_{O_2}	P_{CO_2}	$P_{(CO+O_2)}$	$\frac{-M_{(CO+O_2)}}{N_{(CO+O_2)}}$
0	0	839.7	419.8	419.9	0.0		
0	3	822.2	484.8	402.4	35.0	49.9	7.15
0	7	803.2	346.8	383.4	73.0	44.7	6.42
0	12.5	781.2	304.8	362.4	114.0	40.5	5.86
0	13.0	(659.1)	(299.4)	(359.7)	Liq. air measurement		
0	23.5	745.8	234.0	327.0	184.8	37.1	5.34
1	7.5	727.1	196.6	308.3	222.2	36.2	5.30
1	13.5	715.2	172.8	296.4	246.0	36.2	5.32
2	0.0	697.4	137.2	278.6	281.6	36.4	5.36
2	3.67	691.6	125.6	272.8	293.2	38.5	5.68
2	3.67		Over total period			39.8	*5.86*
				Theory			**6.00**
		In liquid air during this interval					
3	0.0	679.2	100.8	260.4	318.0	17.6	3.1
5	0.0	643.3	29.0	224.5	389.8	34.4	5.14
∞		621.5	0.0	207.1	414.4		

ANALYSIS

Cc. (N. T. P.)	Total	CO	O_2	CO_2
Initial	5.742	2.871	2.871	0.00
Final	4.250	0.000	1.413	2.837
Reacted		2.871	1.458	
Correcting for gas law				
2.837 CO_2 would form from		2.854	1.427	
Unaccounted for		0.017	0.031	

TABLE IV

Reaction: $2CO + O_2 = 2CO_2$. Initially $3CO$ to $1O_2$

Bulb: vol., 5.095 cc.; diam., 2.135 cm. $E_0 = 0.0744$ curie

Time						$(K\mu/\lambda)'$ Calcd. on	
Days	Hours	$P_{(\text{total})}$	P_{CO}	P_{O_2}	P_{CO_2}	$P_{(CO+O_2)}$	$\frac{-M_{(CO+O_2)}}{N_{(CO+O_2)}}$
0	0	861.4	646.0	215.4	0.0		
0	3	835.8	594.8	189.8	51.2	56.6	8.00
0	6.5	812.3	547.8	166.3	98.2	50.0	7.06
0	9.5	795.8	514.8	149.8	131.2	44.6	6.30
0	12.0	783.6	490.4	137.6	155.6	44.0	6.23
0	22.5	744.7	412.6	98.7	233.4	40.0	5.65
1	0.0	(502.3)	(406.6)	(95.7)	Liq. air measurement		
1	6.0	724.1	371.4	78.1	274.6	37.5	5.31
1	6.0		Over total period		426.8	43.6	*6.16*
3	22.5	649.5	220.2	2.5[a]			
				Theory			**6.00**

[a] A faint ring of black appeared in the lower part of the bulb, showing that decomposition of carbon monoxide was beginning. Accidental loss of the gas at this stage prevented analysis.

TABLE V

M/N RATIOS FOR VARIOUS MIXTURES

Ratio, $\frac{CO}{O_2}$	$\frac{-M_{(CO+O_2)}}{N_{CO}}$	$\frac{-M_{(CO+O_2)}}{N_{O_2}}$	$\frac{-M_{(CO+O_2)}}{N_{(CO+O_2)}}$
0.46	19.15	8.1	5.68[a]
1.00	14.95	13.7	7.15
2.00	12.9	23.8	8.38
3.00	10.8	30.5	8.00
4.17	7.1	27.3	5.65[a]

[a] These values are lower than the other three because they are calculated from kinetic measurements made toward the end of the reaction. Even in the stoichiometric mixture the velocity constants drop somewhat in the course of the reaction. The lower values toward the end of the reaction are therefore not attributable to the variation of the ratio of the concentration of the reactants.

The oxidation of carbon dioxide proceeds in mixtures of excess of carbon monoxide and oxygen with the same velocity as in the stoichiometric mixture (Tables II, III and IV), as would be expected from the nearly equal specific ionization of carbon monoxide and oxygen. The velocity constants drop slightly in the course of the reaction. In the case of an excess of carbon monoxide, no free carbon from direct decomposition of carbon monoxide is observed until the oxygen is practically exhausted.

That both carbon monoxide ions and oxygen ions are effective is shown clearly from the lack of constancy of the values of $-M_{(CO + O_2)}/N_{CO}$ and $-M_{(CO + O_2)}/N_{O_2}$ for the various mixtures of the two reactants (Table V), as compared with $-M_{(CO + O_2)}/N_{(CO + O_2)}$, which also is in best agreement with the theoretical value 6.

The oxidation of carbon monoxide was also found to take place at liquid-air temperature, which proves that moisture is not necessary when the action is produced by ionization.[30] The velocity of the reaction at liquid-air temperature is half that at ordinary temperature and possibly the diminution is due to other factors rather than to a true decrease in the M/N ratio. Such factors as the unfavorable position of radon when frozen on the wall, a partial covering of radon by freshly condensed carbon dioxide, etc., would cause slower reaction.

Reduction of Carbon Monoxide by Hydrogen

The reduction of carbon monoxide by hydrogen in a gaseous mixture with radon was examined by Scheuer[31] with reference to the claim of Stoklasa[32] that under the influence of radon, hydrogen and carbon dioxide react in the presence of potassium acid carbonate to form formaldehyde, which polymerizes to reducing sugars. Scheuer found that reaction of

[30] Contrast with the work of Dixon [*Phil. Trans.*, **175A**, 617 (1884)] on the incombustibility of dry carbon monoxide and oxygen.

[31] Scheuer, *Compt. rend.*, **158**, 1887 (1914).

[32] Stoklasa, Sebor and Zdobnicky, *ibid.*, **156**, 646 (1913).

the gases, carbon monoxide and hydrogen resulted in the intermediate reduction to formaldehyde and finally to methane (almost exclusive product). He observed the appearance (excessively feeble) of a solid which later disappeared in the course of the reaction. The reduction was also accompanied by the presence of water, which would be expected if it proceeds to methane. We have been unable to confirm either the calculations or the results of Scheuer's analyses and experiments. We obtain no methane and no water but an abundant white solid which gives the reactions of neither aldehydes nor sugars and is insoluble in water.

Three experiments were carried out with mixtures in which the carbon monoxide and hydrogen were initially 2:1, 1:1 and 1:2, respectively. Carbon monoxide and hydrogen disappeared approximately in 1:1 ratio but the reaction is complicated by the formation of some carbon dioxide and the kinetics indicates that there is back reaction from the solid formed. That both carbon monoxide and hydrogen ions enter into the reaction is shown clearly by Table VI containing M/N ratios for the initial stages of the reaction (compare Table V and its discussion).

TABLE VI

REDUCTION OF CARBON MONOXIDE BY HYDROGEN

Ratio $\frac{H_2}{CO}$	$\frac{-M_{(CO+H_2)}}{N_{(CO+H_2)}}$	$\frac{-M_{(CO+H_2)}}{N_{(CO+H_2)}}$	$\frac{M_{(CO+H_2)}}{N_{H_2}}$
0.5	3.22	3.60	30.9
1.0	2.82	3.48	14.9
2.0	3.55	4.89	10.5

An interpretation of $M/N = 3$ (approached in these experiments) must await further study of this reaction, where the carbon dioxide formed could be removed and determined, thereby eliminating the secondary reaction of carbon dioxide with hydrogen. (See Reduction of Carbon Dioxide.) The back reaction from the solid formed will also be studied.

To illustrate the course of the reaction, data on the 1:1 mixture are given in Table VII.

TABLE VII

Reaction: $CO + H_2 \longrightarrow (H_2CO)_n(?)$. Initially 1CO to 1H$_2$
Bulb: vol., 2.726 cc.; diam., 1.733 cm. $E_0 = 0.1084$ curie

Time			$(K\mu/\lambda)'$ Calcd. on
Days	Hours	$P_{(\text{total})}$	$P_{(\text{total})}$
0	0.0	579.2	
0	17.0	454.2	18.7
1	5.0	400.5	15.3
1	17.0	363.9	12.8
2	5.0	338.4	10.6
2	18.0	315.1	10.5
3	5.5	296.1	11.3
3	21.0	279.3	8.9
4	17.0	263.1	7.9
5	18.0	247.1	7.6
7	0.0	235.9	6.3
8	.0	230.0	5.0
9	19.0	220.0	6.4
12	0.0	212.6	5.6
16	.0	204.7	5.8
		195.9	

TABLE VII (*Concluded*)

ANALYSIS

Cc. (N. T. P.)	Total vol.	CO	H_2	CO_2
Initial	2.077	1.038	1.039	0.000
Final	0.703	0.040	0.383	.280
Reacted		.998	.656	

BALANCE SHEET

	C	H	O
Initial	1.038	2.078	1.038
Gas at end	0.320	0.766	0.600
Out of gas phase	.718	1.312	.438
Empirical formula of solid	$C_{1.64}:H_3:O$		

Decomposition of Carbon Dioxide

Cameron and Ramsay[19] made a preliminary study of the action of radon on carbon dioxide. Where they had expected (by analogy with action of the spark) its decomposition into carbon monoxide and oxygen with increase of volume, they found, in the presence of mercury, a decrease of volume, the appearance of free carbon and oxidation of the mercury. Wourtzel[33] showed that these phenomena were due to the reduction of carbon dioxide by mercury (or phosphorus) and that carbon dioxide in the absence of a reducing agent is but slightly affected by radon. This result in the absence of mercury we have confirmed, but we do not attribute the absence of decomposition to the chemical stability of the carbon dioxide molecule as did Wourtzel. The energy necessary to ionize carbon dioxide is about 10 times that required to decompose it. Its ionization by α-rays is known to be normal and yet Table VIII shows that the decomposition is very slight.

It is possible that the observed decrease in pressure of 1% is due to reduction of carbon dioxide by mercury in the fine capillary (0.2 mm. in diameter) or to slight reaction of carbon dioxide with the glass.

The following hypothesis has been proposed:[34] $CO_2 + [\alpha] = CO_2^+ + (-)$; $CO_2^+ + CO_2 = (CO_2)_2^+$; $(CO_2)_2^+ + (-) = 2CO_2$, which assumes that carbon dioxide behaves ionically just as carbon monoxide, but that the neutralized complex decomposes to carbon dioxide again, with no net

TABLE VIII

CARBON DIOXIDE DECOMPOSITION (PRACTICALLY NEGLIGIBLE)

Bulb: vol., 3.996 cc.; diam., 1.969 cm. $E_0 = 0.1391$ curie

Time		P_{CO_2}		
Days	Hours	Mm. of Hg at 0°	$(K\mu/\lambda)'$	$-M_{CO_2}/N_{CO_2}$
0	0	605.9		
40	21.5	599.4	0.0662	5.4×10^{-3}

Analysis of final gas gave 99.9% of CO_2

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[33] Ref. 6, p. 346.

[34] Ref. 12 b, p. 67.

result. To test this hypothesis we attempted to arrest the reversal by means of some "acceptor" which would react chemically with CO_2^+. We chose hydrogen as probable, which Wourtzel had also predicted from analogy with the action of mercury on ionized carbon dioxide. Rapid reaction was disclosed, as will be shown in the following section.

Reduction of Carbon Dioxide by Hydrogen

Data for four experiments starting with mixtures of carbon dioxide and hydrogen in different proportions are reported in Tables VIII, IX, X and XI. The balance sheet at the end of the tables shows that two molecules of carbon dioxide react with about five molecules of hydrogen. In each case, some carbon monoxide is found in the final gaseous mixture. Water and compounds containing carbon, hydrogen and oxygen are formed.

The velocity constants $(k\mu/\lambda)'$ drop very rapidly during an experiment in mixtures with an excess of carbon dioxide (see Tables VIII and IX). However, the velocity constants over the first period for the four experiments lead to values of $-M_{(CO_2 + H_2)}/N_{(CO_2 + H_2)}$ quite approximately equal to 1.65 as shown in Table XII even though the ratio of hydrogen to carbon dioxide is varied eight-fold. A qualitative explanation for the low value and the drop of the velocity constants during an experiment was proposed by one of us,[34] in which it was suggested that encounters of CO_2^+ with CO_2 destroy its activity just as though hydrogen were not present. Although this theory is supported by the data for a 1:1 carbon dioxide-hydrogen mixture (Table X), it does not yield a satisfactory interpretation for the velocity in the other hydrogen-carbon dioxide mixtures, and the approximate constancy of $-M_{(CO_2 + H_2)}/N_{(CO_2 + H_2)}$ for the initial step of the reaction, even though the ratio of hydrogen to carbon dioxide is variant, is not in accord with this hypothesis.

Values of $-M_{(CO + H_2)}/N_{CO_2}$ and $-M_{(CO + H_2)}/N_{H_2}$, shown in Table XIII, Cols. 3 and 4, prove conclusively that the reaction is not brought about by active hydrogen alone, but that both CO_2^+'s and H_2^+'s are effective (compare also Tables V and VI).

It is evident that in the reduction of carbon dioxide by hydrogen, as in the reduction of carbon monoxide by hydrogen, the reaction is disturbed along its course. There may be back or side reactions with the products. To eliminate these disturbing factors, it may be possible to radiate the mixture with radon confined in an α-ray bulb and circulate the gases with the products through low-temperature traps where the products can be removed from the field of radiation.

The result of the reaction of carbon dioxide and hydrogen under α-radiation recalls the earlier work with electric discharge[35] which gave

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[35] Losanitch and Jovitchitch, *Ber.*, **30**, 136 (1897). Moser and Isgarichew, *Z. Elektrochem.*, **16**, 613 (1910).

similar products. The recent work of Lunt[36] is of great interest in showing that the high-frequency corona gives other products, namely, the water-gas equilibrium and also methane under some conditions.

Table IX

Reaction: $CO_2 + 2H_2 \longrightarrow (H_2O) + (H.CHO)_n(?)$. Initially $2CO_2$ to $1H_2$
Bulb: vol., 4.219 cc.; diam., 2.005 cm. $E_0 = 0.1066$ curie

Time Days	Hours	$P_{\text{(total)}}$ (dry)	P_{CO_2}	P_{H_2}	P_{CO}	$(K\mu/\lambda)'$ Calcd. on $P_{\text{(total)}}$
0	0	751.9	501.3	250.6	0.0	
0	8	685.0	475.7	205.3	4.0	15.1
0	19	626.5	453.3	165.7	7.5	11.2
1	9	569.9	431.6	127.4	10.9	10.3
1	19	540.5	420.4	107.5	12.6	8.8
2	7	513.6	410.1	89.3	14.2	7.7
2	19	492.3	402.0	74.9	15.4	6.9
3	7	475.3	395.5	63.4	16.4	6.4
3	22	461.6	390.3	54.1	17.2	4.7
4	20	448.3	385.2	45.1	18.0	3.7
6	19	432.8	379.3	34.6	18.9	2.66
10	0	423.7	375.9	28.4	19.4	1.54
14	0	417.5	373.3	24.2	20.0	1.65
		409.6	370.3	18.9	20.4	2.22

Analysis

Cc. (N. T. P.)	Total	CO_2	H_2	CO
Initial	4.174	2.783	1.391	0.0
Final	2.273	2.055	0.105	.113
Reacted		0.728	1.173	

Balance Sheet

	C	H	O
Initial	2.783	2.782	5.566
As gases at end	2.168	0.210	4.223
Out of gas phase	0.615	2.572	1.343

$C:H_{4.18}:O_{2.8}$

Table X

Reaction: $CO_2 + H_2 \longrightarrow (H_2O) + (H_2CO)_n(?)$. Initially $1CO_2$ to $1H_2$
Bulb: vol., 4.330 cc.; diam., 2.022 cm. $E_0 = 0.1008$ curie

Time Days	Hours	$P_{\text{(total)}}$ (dry)	P_{CO_2}	P_{H_2}	P_{CO}	$(K\mu/\lambda)'$ Calcd. on $P_{\text{(total)}}$
0	0	656.6	328.3	328.3	0.0	
0	16.25	578.9	302.9	271.8	4.2	10.9
1	5.6	531.4	287.4	237.3	6.7	10.1
1	20.0	488.9	273.5	206.4	9.0	10.1
2	5.83	465.8	265.9	189.6	10.3	9.4
3	3.25	424.5	252.4	159.6	12.5	9.3
4	5.83	390.8	241.4	135.1	14.3	8.0
5	17.25	360.5	231.5	113.1	15.9	7.4

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[36] Lunt, *Proc. Roy. Soc.*, **108**, 172 (1925).

TABLE X (*Concluded*)

Time		$P_{(\text{total})}$ (dry)	P_{CO_2}	P_{H_2}	P_{CO}	$(K\mu/\lambda)'$ Calcd. on $P_{(\text{total})}$
Days	Hours					
6	22.75	343.1	225.7	100.4	17.0	6.9
8	16.00	325.7	220.0	87.8	17.9	6.8
11	18.5	307.1	213.9	74.3	18.9	6.5
18	0.0	290.8	208.6	62.4	19.8	6.6
		282.8	206.0	56.6	20.2	8.0

ANALYSIS

Cc. (N. T. P.)	Total	CO_2	H_2	CO
Initial	3.740	1.870	1.870	0.0
Final	1.612	1.174	0.323	.115
Reacted	2.128	0.696	1.547	

BALANCE SHEET

	C	H	O
Initial	1.870	3.740	3.740
As gases at end	1.289	0.646	2.463
Out of gas phase	0.581	3.094	1.277

Empirical ratio $C:H_{5.31}:O_{2.2}$

TABLE XI

Reaction: $CO_2 + H_2 \longrightarrow (H_2O) + (H_2CO)_n(?)$. Initially $1CO_2$ to $2H_2$
Bulb: vol., 5.690 cc.; diam., 2.213 cm. $E_0 = 0.235$ curie

Time		$P_{(\text{total})}$ (dry)	P_{CO_2}	P_{H_2}	P_{CO}	$(K\mu/\lambda)'$ Calcd. on $P_{(\text{total})}$
Days	Hours					
0	0	837.1	279.0	558.1	0.0	
0	13.25	731.0	246.6	482.5	1.9	7.04
0	17.0	708.9	239.9	466.7	2.3	6.00
0	20.5	689.5	234.0	452.9	2.6	6.00
1	13.0	614.2	211.0	399.2	4.0	5.7
1	20.5	586.2	202.5	379.3	4.4	5.5
2	13.0	536.8	187.5	344.1	5.2	5.2
2	20.5	519.6	182.2	331.8	5.6	4.75
3	14.0	486.1	172.2	307.9	6.0	4.5
4	13.0	450.6	161.5	282.6	6.5	4.5
5	19.0	415.6	150.8	257.6	7.2	4.5
7	20.0	378.4	139.2	231.1	8.1	4.25
13	14.25	329.1	124.2	195.9	9.0	4.35
		304.3	116.2	178.2	9.9	4.35

ANALYSIS

Cc. (N. T. P.)	Total	CO_2	H_2	CO
Initial	6.265	2.088	4.177	0.0
Final	2.277	0.870	1.333	.074
Reacted		1.218	2.844	

BALANCE SHEET

	C	H	O
Initial	2.088	8.354	4.176
Gases at end	0.944	2.666	1.814
Out of gas phase	1.144	5.688	2.362

$C:H_{5.0}:O_{2.1}$

TABLE XII

Reaction: $CO_2 + H_2 \longrightarrow (H_2O) + (H_2CO)_n(?)$. Initially $1CO_2$ to $4H_2$
Bulb., vol., 3.127 cc.; diam., 1.814 cm. $E_0 = 0.0910$ curie

Time		$P_{(total)}$ (dry)	P_{CO_2}	P_{H_2}	P_{CO}	$(K\mu/\lambda)'$ Calcd. on $P_{(total)}$
Days	Hours					
0	0	657.7	131.5	526.2	0.0	
0	21	594.3	109.2	481.6	3.5	7.7
1	21	556.9	96.1	455.2	5.6	5.1
2	22	530.2	86.7	436.4	7.1	4.4
4	22	495.2	74.4	411.7	9.1	4.2
7	8	469.8	65.4	393.9	10.5	4.0
12	0	446.7	57.3	377.6	11.8	3.7
		428.2	50.8	364.5	12.9	4.0

ANALYSIS

Cc. (N. T. P.)	Total	CO_2	H_2	CO
Initial	2.710	0.542	2.168	
Final	1.760	.209	1.498	0.053
Reacted		.333	0.670	

BALANCE SHEET

	C	H	O
Initial	0.542	4.336	1.084
Gas at end	.262	2.996	0.471
Out of gas phase	.280	1.340	.613

$C:H_{4.8}:O_{2.2}$

TABLE XIII

Ratio $\frac{H_2}{CO_2}$	$\frac{-M_{(CO_2+H_2)}}{N_{(CO_2+H_2)}}$	$\frac{-M_{(CO_2+H_2)}}{N_{CO_2}}$	$\frac{-M_{(CO_2+H_2)}}{N_{H_2}}$
0.5	1.75	1.86	56.5
1.0	1.63	1.98	24.8
2.0	1.66	2.17	14.2
4.0	1.65	2.75	8.2

Discussion of Results

The conclusions in this and the preceding papers as to the chemical behavior of gaseous ions have been drawn from experiment rather than from theoretical considerations. The amount of chemical action is measured either directly by chemical analysis or by following the course of the change of pressure and controlling its interpretation by chemical analysis after completion of the reaction. The interpretation of pressure change has also been aided when necessary by the employment of low temperature (down to —191°) to freeze out one or more components.

Since our conclusions as to the behavior of gaseous ions were originally made deductively with little physical basis, it is interesting to see how this earlier chemical evidence accords with later physical theories and experiment. In a very important paper in 1924, J. J. Thomson[8] treated the subject of the chemical behavior of gaseous ions electrodynamically.

His conclusions agree, in most cases, with the results of the α-ray experiments, though he used for comparison only the meager and much less suitable examples of the chemical effects of X-rays. It remains, therefore, for us to undertake a comparison between Thomson's deductions from electrodynamic theory and the experimental α-ray results.

Thomson's main conclusion that gaseous ionization may produce chemical reaction in the proportion of one or a few molecules per ion pair is identical with that of Lind's first paper[3] in 1912 and of all the later ones. In the present paper it has been shown that the two factors which may raise the M/N value by a few integers above unity are: *clustering* of neutral molecules about ions, and the equality of action of positive and *negative* ions. Both of these principles are deduced by Thomson. The negative ions have so far been found active by us only when oxygen is present, but in those cases the doubling of the reaction is so striking as to lead to the necessity of assuming that the O_2^- is equally effective with the positive ions in furnishing clustering centers for chemical action. Therefore the assumption of this equality which was made to fit experimental results without reference to the physical properties of negative ions becomes tremendously strengthened by Thomson's electrodynamic basis.

The work of Loeb, of Wahlin and of Erikson, both on clustering and on the formation of negative ions from free electrons, has been discussed in another paper[12b] in this same connection. In treating clustering or the formation of complex ions Thomson concluded that collision between ions and neutral molecules will lead to momentary complexes which will continue to form and again dissociate as long as the ions persist. Our experiments appear to throw some light on this. If any ions be neutralized by combination with those of opposite sign at a moment when the clusters have less than the number of molecules necessary to complete the chemical reaction, the efficiency will be thereby reduced. But since experimentally we find that the ionic reactions have a high percentage of theoretical efficiency, either the clusters do not dissociate as according to Thomson, or else the duration in the dissociated state must be very short compared with the average life of the complex.

The question arises as to how many neutral molecules are carried into a chemical reaction through association in the ionic complex. While no definite answer can be given, it is quite surprising how frequently this number corresponds to the simple formulation of the chemical reaction in terms of whole molecules for both the negative and positive ions. For example, we write $2H_2 + O_2 = 2H_2O$, or $2CO + O_2 = 2CO_2$, and correspondingly we find double this quantity of action for an ion pair and hence assume that the positive ion cluster consists of the number of molecules indicated on the left-hand side of each equation and that the negative ion cluster is composed of the same number. Possibly the clusters are really larger and upon neutralization the other molecules slough off without reacting. The smallest number usually reacts which will satisfy the simplest valence requirements.

It remains to review and modify one or two of the earlier statements in regard to these gas-ion reactions. In the paper by one of us on "The Electrochemistry of Gases," in 1923 it was stated[37] "ions do not interact nor do molecules or atoms otherwise activated interact. Their momentary concentrations are too low. They react only with neutral or unactivated molecules." At least with respect to ions we now believe that the final chemical reaction takes place only when the positive and negative clusters (or the positive cluster and free electrons) come together and neutralize each other. But the low momentary concentration does prevent interaction *before they have had time to cluster with other neutral* molecules.

The aspect of the "Faraday equivalence" involved in the ionic-chemical reactions should be referred to again.[38] Stress was earlier laid on this in order to bring out clearly that the reactions are not *catalytic* in the ordinary sense, but that a definite quantity of chemical reaction is associated with a definite number of ions just as in electrolysis. It was predicted and is now definitely known that the equivalence is by no means the same as in electrolysis. The ions are merely the collecting centers of a definite number of molecules, but the valences involved in the chemical reactions exceed by several fold the free ionic charges. In this, some resemblance to catalysis is seen, but the great difference is that the ions themselves enter into the reaction and are destroyed by it so that their activating influence is not multiplied by any "chain" or catalytic mechanism.

The fact that when the partial pressure of the reactants becomes only a small fraction of the total pressure through the generation of some other gaseous product, nevertheless the reaction still "weaves its way" undisturbed kinetically and ionically is remarkable. For example, the oxidation of carbon monoxide by oxygen illustrates the point well. Even when the partial pressure of the carbon dioxide generated predominates, it seems neither to accelerate nor to retard the reaction, although carbon dioxide is being ionized normally.

It is a pleasure to acknowledge the coöperation of Drs. A. G. Loomis and J. H. Perry, and Messrs. J. E. Walters and F. Porter of the Cryogenic Laboratory of the Bureau of Mines in the low-temperature manipulations and measurements involved in these experiments.

Summary

1. The chemical reactions taking place in gases mixed with radon have been followed by means of the pressure changes at ordinary and low

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[37] Ref. 12 b, p. 70.

[38] Lind. *Z. physik. Chem.*, **84**, 759 (1913).

temperatures and have been controlled by final chemical analysis of the gaseous products. The ratio of the number (M) of molecules reacting to the number (N) of ion pairs produced in the reactants by α-radiation has been established, which in some cases gave a satisfactory interpretation of the reaction mechanism. The reactions studied are: decomposition of carbon monoxide and of carbon dioxide (negative result); reduction by hydrogen of carbon monoxide and of carbon dioxide; and the oxidation of carbon monoxide by oxygen.

2. In the decomposition of carbon monoxide the ratio ($-M_{CO}/N_{CO}$) approximates the value 2, but is slightly higher initially and shows a tendency to diminish in the later stages of the reaction. Besides the products, carbon dioxide and carbon, a substance, apparently a sub-oxide of carbon, is deposited on the wall in an even film. The ratio of carbon monoxide (disappearing) to carbon dioxide (forming) is 3:1, but the proportion of sub-oxide to carbon has not yet been determined.

3. Carbon monoxide is oxidized by oxygen under α-radiation. The ratio found, $-M_{(CO + O_2)}/N_{(CO + O_2)} = 6$, is interpreted to mean that both negative and positive clusters are formed, $(CO.O_2.CO)^{+ \text{ or } -}$ from CO^+ or O_2^+ or O_2^- (not from CO^-) and react as $(CO.O_2.CO)^+ + (CO.O_2.CO)^- = 4CO_2$. The reaction proceeds practically independently of the carbon dioxide produced.

4. The reaction $2CO + O_2 = 2CO_2$ was found to proceed at liquid-air temperature with half the velocity at 25°, proving that moisture is not necessary for the *ionic* reaction.

5. Carbon monoxide and hydrogen combine at ordinary temperature under α-radiation to form a white, solid substance which has not been identified. Its composition is approximately that of a polymer of formaldehyde. The ratio $-M_{(CO + H_2)}/N_{(CO + H_2)} = 3$ has not been interpreted.

6. Carbon dioxide is not decomposed chemically by α-radiation. Ionic reaction is assumed as follows: $CO^+ + CO_2 = (CO_2.CO_2)^+$; and $(CO_2.CO_2)^+ + (-) = 2CO_2$.

7. Mixtures of hydrogen and carbon dioxide react, forming water and probably carbohydrates (not identified), and a very small proportion of carbon monoxide, but no methane.

8. The M/N ratios for various mixtures of carbon dioxide and hydrogen or carbon monoxide and hydrogen and of carbon monoxide and oxygen prove that in all three cases (as also in water formation, Part I) the ions of both reactants are chemically active.

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