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Joseph O. Hirschfelder and Hugh S. Taylor

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The Alpha-Particle Reactions in Carbon Monoxide, Oxygen and Carbon Dioxide Systems

JOSEPH O. HIRSCHFELDER
Department of Chemistry, University of Wisconsin, Madison, Wisconsin

AND

HUGH S. TAYLOR
Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

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The methods developed by Eyring, Hirschfelder and Taylor for the analysis of the alpha-particle reactions in hydrogen and hydrogen-bromine systems have been extended to the corresponding reactions in carbon monoxide, oxygen, and carbon-dioxide systems and to mixtures of these gases. It has been shown that experimentally known processes of ionization and of excitation, together with the probable neutralization processes, with consequent chemical reactions involving the atomic species so produced, suffice to account quantitatively for the observed experimental results. This extends the scope of the method employed to typical alpha-particle reactions of decomposition, ozonization and oxidation hitherto interpreted in terms of a clustering mechanism.

IN studying, with Eyring, the ortho-para-hydrogen conversion and the synthesis and decomposition of hydrogen bromide under the influence of alpha-particles, we came to the conclusion that the ionization occurring in hydrogen, under such conditions, eventually produced from 3 to 4 hydrogen atoms per ion pair produced in the system. Further, we concluded that, to the extent that molecular excitation processes in the track of the alpha-particle occur, these minimum yields of atomic hydrogen will be exceeded. From our analysis of the data of Lind and Livingston on the hydrogen-bromine-hydrogen bromide reaction we concluded that the total yield from ionization and molecule excitation may reach 6 hydrogen atoms measured in terms of ion pairs produced.[1–3]

The experimental demonstration of reaction due to the excitation of molecules, in addition to ionization, by alpha-particles has recently been achieved by Smith and Essex.[4] They have shown that, in the decomposition of ammonia by alpha-rays, as much as two-thirds of the total reaction is due to mechanisms other than those involving ions and their recombination. This research can be recorded as supporting the additional formation of atomic hydrogen which we found it necessary to assume in our previous studies. To test our conclusions, Mund and van Tiggelen,[5] in 1937, undertook to find the number of hydrogen atoms, per ion pair, produced by an alpha-particle in hydrogen containing a small amount of hydrogen sulfide. They measured the number of molecules of hydrogen sulfide disappearing per ion pair. In two series of data they found mean values of 2.14 and 2.2, respectively, with extreme values of 3.16 and 1.7. They assumed the reactions to be $H+H_2S \rightarrow H_2+HS$ followed by $2HS=H_2+S_2$, following a mechanism agreeing with photochemical quantum yield measurements of Stein.[6] A quite recent research by Forbes, Cline and Bradshaw[7] indicates, however, that the quantum yield is 1.02 ± 0.05 molecules of hydrogen per quantum, independent of pressure over the range 8–1400 mm, and of light intensity over a fourteen-fold range. They are thus led to a mechanism $H+H_2S \rightarrow H_2+HS$ followed by $HS+HS=H_2S+S$ from which it would follow that the Mund-van Tiggelen data indicate mean yields of 4.28 and 4.4 with individual determinations indicating as high as

[1] Eyring, Hirschfelder and Taylor, J. Chem. Phys. **4**, 479 (1936).
[2] Eyring, Hirschfelder and Taylor, J. Chem. Phys. **4**, 570 (1936).
[3] Lind and Livingston, J. Am. Chem. Soc. **58**, 612 (1936).
[4] Smith and Essex, J. Chem. Phys. **6**, 188 (1938).
[5] Mund and van Tiggelen, Bull. Soc. Chim. Belg. **46**, 129 (1937).
[6] Stein, Trans. Faraday Soc. **29**, 583 (1933).
[7] G. S. Forbes, Cline and Bradshaw, J. Am. Chem. Soc. **60**, 1431 (1938).

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6.3 atoms of hydrogen per ion pair. This modification of the Mund-van Tiggelen results brings the work on alpha-particles in hydrogen-hydrogen sulfide mixtures into good agreement with our computations in the ortho-parahydrogen reaction and the hydrogen bromide synthesis.

Quite recently Gunther has re-examined[8] his earlier data[9] on the hydrogen-chlorine reaction under ionizing influences and has concluded that they can better be reconciled with our theory of such processes than with the "cluster-theory" on which his earlier interpretation was based. He shows, further, that new experiments on the decomposition of azomethane under ionization cannot be reconciled with the cluster theory but require such a treatment as we have given for their interpretation.

The cumulative effect of these several researches in support of our theoretical analysis of the alpha-ray reactions in hydrogen-containing systems encourages us to present our analysis of the alpha-particle reactions in the systems carbon monoxide, carbon dioxide and oxygen. The system carbon monoxide-oxygen can be employed to illustrate the general applicability of our methods to oxidation processes under ionization conditions.

Any theory which is proposed for the radiochemical oxidation of carbon monoxide must explain the following experimental facts. Carbon dioxide is the sole product[10–13] of alpha-particle bombardment of carbon monoxide-oxygen mixtures. The yield is practically independent of the ratio of the two reactants until these species approach exhaustion, and four molecules of carbon dioxide are formed per ion pair produced by impact of alpha-particles with the reactants. Radiation absorbed by the carbon dioxide has little effect on the reaction kinetics and the reaction proceeds at a rate influenced to only a minor degree by the ions produced by impact of alpha-particles with the carbon dioxide product. The oxidation process under ionizing influence continues even with the reaction bulb immersed in liquid air.

Pure carbon dioxide, under alpha-radiation, remains practically unchanged, and the ion efficiency is practically zero. With pure carbon monoxide, about two molecules of carbon monoxide disappear per ion pair formed. Carbon suboxide is deposited, and carbon dioxide appears equal to about two-thirds of that required by a reaction $2CO = CO_2 + C$. The empirical formula of total solid deposited is C_2O. Pure oxygen, under alpha-ray ionization, yields ozone with low yields in static systems, reaching at least 1 to 1.25 molecules of ozone per ion pair in flow systems.[14] Lind and Bardwell[15] found 1.7 molecules of ozone per ion pair and two results in excess of 2 were obtained in flow systems. The yield is evidently dependent on the reverse process of de-ozonization.

We now proceed to an analysis of these experimental data, resolving the total process into three component parts, (a) the ionization and excitation processes caused by the alpha-particle and its secondary electrons, (b) the neutralization process and the reactive species thus produced, and (c) the chemical reactions which such species may induce. We consider first these several stages in the several pure gases and then we shall consider gaseous mixtures of the three.

I. Radiochemical Reactions in Pure Carbon Monoxide

1. Ionization processes

Excellent investigations are available of the processes of ionization, excitation and negative ion formation in carbon monoxide from mass-spectrographic data of the products formed in electrical discharges[16–20] and from the data of electron impacts of controlled speeds.[21] In electrical discharges, the ions CO^+, C^+ and CO^{++}

[8] P. Gunther and H. Theobald, Zeits. f. physik. Chemie **B40**, 1 (1938).
[9] P. Gunther and G. Cohn, Zeits. f. physik. Chemie **B26**, 8 (1934); P. Gunther and K. Holm, *ibid.* **B33**, 407 (1936).
[10] S. C. Lind, *Chemical Effects of Alpha-Particles* (Chemical Catalog Co., 1928), p. 165.
[11] S. C. Lind and D. C. Bardwell, J. Am. Chem. Soc. **47**, 2675 (1925).
[12] S. C. Lind and C. Rosenblum, Proc. Nat. Acad. Sci. **18**, 374 (1932).
[13] C. Rosenblum, J. Am. Chem. Soc. **55**, 220 (1933).
[14] J. D'Olieslager, Bull. Acad. Roy. Belg. **12**, 719 (1925).
[15] S. C. Lind and D. C. Bardwell, J. Am. Chem. Soc. **51**, 2751 (1929).
[16] Hogness and Harkness, Phys. Rev. **32**, 936 (1928).
[17] Kallmann and Rosen, Zeits. f. Physik **61**, 61 (1930).
[18] H. D. Smyth, Rev. Mod. Phys. **3**, 347 (1931).
[19] A. L. Vaughan, Phys. Rev. **38**, 1687 (1931).
[20] W. W. Lozier, Phys. Rev. **46**, 268 (1934).
[21] Savard, de Hemptinne and Capron, Comptes rendus **204**, 354, 1039 (1937).

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are all found, but CO^+ ions, at the low pressures of these experiments, were of the order of 1000 to 100 times more numerous than the other species. Thus, the primary ionization is, in major part,

$$CO = CO^+ + \epsilon - 13.5 \text{ ev.} \quad (1)$$

The energy consumed, 13.5 ev, is derived from the electron impact data. The same source indicates that, at 16.1 ev and 19.1 ev, two excited states of the CO^+ ion may be formed, while the direct formation of $C^+ + O$ requires 20 ev. For the dissociation of the carbon monoxide molecule into neutral atoms, Savard, de Hemptinne and Capron deduce an energy of 8.8 ev. Faltings, Groth and Harteck, in a review of the spectroscopic data, coupled with their own observations of the photodissociation of carbon monoxide,[22] conclude that, at present, the most reliable value is that given by Herzberg,[23] 9.097 ev. Hogness and Harkness obtained good evidence that an ionic reaction occurs:

$$CO^+ + CO = C^+ + CO_2. \quad (2)$$

However, a simple calculation shows that this reaction will require excited CO^+ ions:

$$\begin{aligned} CO^+ + \epsilon &= CO + 13.5 \text{ ev} \\ CO &= C + O - 9.1 \text{ ev} \\ C &= C^+ + \epsilon - 11.3 \text{ ev} \\ CO + O &= CO_2 + 5.5 \text{ ev} \\ \text{whence} \quad CO^+ + CO &= C^+ + CO_2 - 1.4 \text{ ev.} \end{aligned}$$

The excited state formed at 16.1 ev would convert this endothermic process to an exothermic one. Experimentally, it would be difficult to determine how much of the CO^+ current is due to each of the three states of the species and, therefore, we cannot make any estimate of the frequency with which the reaction (2) forming C^+ and CO_2 occurs. Since Hogness and Harkness were able to distinguish the reaction at pressures lower than 1 mm Hg, it must occur frequently at atmospheric pressure.

2. Excitation processes

These are known through the absorption spectra observed in the ultraviolet by Hopfield and Birge[24] and by Leifson.[25] There are a large number of excited states of carbon monoxide but, when the molecule dissociates, a normal carbon and a normal oxygen atom are produced,

$$CO \rightarrow C + O - 9.1 \text{ ev.} \quad (3)$$

The energy consumed is taken as 9.1 ev as indicated above, but the exact magnitude does not concern us here.

3. Negative ion formation

The formation of negative ions in carbon monoxide has been investigated by Wahlin,[26] Bradbury,[27] Tate and Lozier,[28] and Lozier.[20] All concur in the conclusion that the carbon monoxide molecule has negligible electron affinity. No negative ions are formed in it until the energy of the impacting electron exceeds 19.5 volts. Savard, de Hemptinne and Capron[21] assign a value of 21.4 ev to the reaction

$$CO + \epsilon = C^+(^4P) + O^- + \epsilon. \quad (4)$$

Lozier arrives at a value of 20.9 ev for the same process, and, for the reaction,

$$CO + \epsilon = C + O^-, \quad (5)$$

a value of 9.5 ev. In the radiochemical reaction, where the available energy is great, both (4) and (5) are possible. However, when Lozier plots the ion currents of CO^+, O^- and C^+ as a function of the electron energy, it appears that the magnitude of the O^- current is of the order of 10^{-3} of the positive ion current. Therefore, we conclude that, whilst negative ions are formed, the number of them is negligible for our purposes.

4. The total processes and chemical reactions

The alpha-particle and its fast secondary electrons use about 30 ev in producing each ion pair. We know that 13.5 ev is used up in reaction (1). The remainder is principally consumed in reaction (3) and unfruitful excitation processes. Thus, the primary stage yields,

$$2CO + \alpha = CO^+ + \epsilon + C + O + \alpha. \quad (6)$$

[22] K. Faltings, W. Groth and P. Harteck, Zeits. f. physik. Chemie **B41**, 15 (1938).
[23] G. Herzberg, Chem. Rev. **20**, 145 (1937).
[24] J. J. Hopfield and R. T. Birge, Phys. Rev. **29**, 922 (1927).
[25] S. Leifson, J. Astrophys. **63**, 82 (1926).
[26] H. B. Wahlin, Phys. Rev. **19**, 173 (1922).
[27] N. Bradbury, J. Chem. Phys. **2**, 827 (1934).
[28] J. T. Tate and W. Lozier, Phys. Rev. **39**, 254 (1932).

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There is a certain chance, w, that the CO^+ will undergo reaction (2). Hence,

$$wCO^+ + wCO = wC^+ + wCO_2. \quad (7)$$

The possible neutralization processes are given in the following equations:

$$CO^+ + \epsilon = C + O \quad (8)$$

$$C^+ + \epsilon + CO = 2C + O. \quad (9)$$

The neutralization of CO^+ will yield a carbon and an oxygen atom, the excess energy appearing either as excitation energy of the atoms or as mutual kinetic energy. The neutralization of C^+ might be expected to yield a carbon atom. However, the energy of this process would have to be emitted in the form of radiation and such radiation processes are of small probability. We, therefore, indicate a neutralization process involving a simultaneous collision with a molecule which, in this case, must be carbon monoxide. Reaction (9) is favorable since not more than 2.5 ev excess energy remain to be converted into the kinetic energy of the fragments.

After the neutralization processes, we therefore obtain, for each ion pair formed in the carbon monoxide,

$$2(1+w)CO + \alpha = wCO_2 + 2O + (2+w)C.$$

The excess of atomic carbon is the origin of the carbon suboxides found in the experimental observations. Some carbon atoms may reach the vessel walls to form solid carbon. Others, doubtless the major portion, react with monoxide to form suboxide, $C + 2CO = C_3O_2$ which polymerizes on the wall. The oxygen atoms can combine with carbon monoxide to form carbon dioxide. The work of Jackson[29] and of Groth[30] has shown this to be a slow three-body process, forty times slower than the three-body reaction $O + O_2 + M \rightarrow O_3 + M$. Oxygen atoms can oxidize either the carbon suboxide or the solid carbon. It is therefore impossible to predict the ratio of the products obtained but the analysis shows definitely that, in nature, they are as experimentally found, and that in the neighborhood of two molecules of carbon monoxide will disappear per ion pair formed. This analysis of the ion reaction is in best agreement with the results of the recent research by Faltings, Groth and Harteck[22] who found that carbon monoxide, dissociated photochemically by light of wave-length $\lambda = 1295$A, causes the decomposition of one molecule of carbon monoxide per absorbed quantum and a similar distribution of reaction products between carbon dioxide and carbon suboxide.

[29] W. F. Jackson, J. Am. Chem. Soc. **56**, 2631 (1934).
[30] W. Groth, Zeits. f. physik. Chemie **B37**, 315 (1937).

II. Radiochemical Reactions in Pure Carbon Dioxide

1. Ionization processes

In carbon dioxide, these processes have been studied by Smyth and Stueckelberg,[31] Kallmann and Rosen,[32] and reviewed by Smyth.[18] The ions CO_2^+, CO^+, O^+ and C^+ are found. At low pressures and moderately high voltages, the relative numbers are of the order 100, 20, 7 and 3, respectively. We shall treat the ions CO_2^+ and CO^+. They are formed in the reactions,

$$CO_2 + \epsilon = CO_2^+ + 2\epsilon - 14.4 \text{ ev} \quad (10)$$

$$CO_2 + \epsilon = CO^+ + O + 2\epsilon - 20.4 \text{ ev}. \quad (11)$$

There is some evidence for the exchange reaction,

$$CO + CO_2^+ = CO^+ + CO_2, \quad (12)$$

and its reverse, in mixtures of the two gases. This does not involve any large energy change since the ionization potentials differ by a fraction of a volt. We shall discuss, later, the possibility of this reaction in connection with the effect of carbon dioxide on the carbon monoxide oxidation.

2. Excitation processes

The ultraviolet absorption spectrum has been studied by Leifson[25] and by Lyman.[33] Bonhoeffer and Harteck[34] conclude from the data that the continuous absorption spectrum corresponds to a dissociation into carbon monoxide and a normal oxygen atom

$$CO_2 = CO + O - 5.5 \text{ ev}. \quad (13)$$

[31] H. D. Smyth and E. C. G. Stueckelberg, Helv. Phys. Acta **2**, 303 (1929); Phys. Rev. **36**, 472 (1930).
[32] Kallmann and Rosen, Zeits. f. Physik **58**, 52 (1929); **61**, 61 (1930).
[33] Lyman, *Ultraviolettspektroscopie*, cited by Bonhoeffer and Harteck.
[34] Bonhoeffer and Harteck, *Grundlagen der Photochemie* (T. Steinkopff, Dresden and Leipzig, 1933), p. 133.

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3. Negative ion formation

Loeb,[35] Wahlin[26] and Bradbury and Tatel[36] find that carbon dioxide does not have an appreciable electron affinity and no negative ions were observed even at the highest electron velocities attained. There is a possibility that some O^- ions might be formed for electron velocities in excess of the 5.5 ev required to dissociate carbon dioxide to carbon monoxide and oxygen. It is, however, evident that the process

$$CO_2+\epsilon=CO+O^- \tag{14}$$

only occurs infrequently.

4. The total processes and chemical reactions

The majority of the positive ions are formed through reaction (10). Let p represent the fraction of times that reaction (11) occurs. There is enough energy available per ion pair formed that reaction (13) can take place with a probability equal to that of positive ion formation. On this basis, for each ion pair produced, we have

$$2CO_2+\alpha=(1-p)CO_2^++pCO^+ +(1+p)O+CO+2\epsilon+\alpha. \tag{15}$$

The neutralization processes will, in this case, be simply

$$CO^++\epsilon=C+O \tag{16}$$

$$CO_2^++\epsilon=CO+O. \tag{17}$$

The neutralization of CO_2^+ to yield three atoms is impossible, requiring 15.5 ev where only 14.4 ev are available. Thus, for each ion pair,

$$2CO_2+\alpha=(2-p)CO+(2+p)O+pC. \tag{18}$$

Under the conditions of the experiment, the carbon atoms will be oxidized by the carbon dioxide present. Lind[37] cites experimental evidence of the oxidation of suboxide in presence of pure carbon dioxide. We have also seen that the recombination of oxygen atoms and carbon monoxide is a slow process. Some of these atoms will therefore reach the wall and undergo two competitive heterogeneous reactions

$$O+O=O_2 \tag{19}$$

$$O+CO=CO_2, \tag{20}$$

the latter also occurring as a three-body gas reaction.[30] When the concentration of O_2 becomes appreciable, the oxygen will act as catalyst for the recombination of CO and O

$$O+O_2=O_3 \tag{21}$$

$$O_3+CO=CO_2+O_2. \tag{22}$$

Both these reactions are reasonably fast. Thus, under the influence of alpha-particles, an equilibrium state between CO_2 and $CO+O_2$ is reached after a small quantity of molecular oxygen is formed in the reaction vessel. It is, therefore, easy to understand the experimental observation that, when alpha-particles pass through pure carbon dioxide gas, there is no appreciable decomposition of the gas.

III. Radiochemical Reactions in Pure Oxygen

1. Ionization processes

Three primary processes are of importance:[38,39]

$$O_2=O_2^++\epsilon-12.5 \text{ ev} \tag{23}$$

$$O_2=O_2^{+\prime}+\epsilon-16.1 \text{ ev} \tag{24}$$

$$O_2=O^++O+\epsilon-19.5 \text{ ev}. \tag{25}$$

There is no evidence for secondary reactions in oxygen or for the formation of complex ions of the type O_3^-.

2. Excitation processes

From spectral data[34] it is seen that the most important transitions are $^3\Sigma_g^-$ to $^3\Sigma_u^-$. When the latter is excited it decomposes to a ^3P and a $'D$ oxygen atom

$$O_2\rightarrow O(^3P)+O('D)-7.05 \text{ ev}. \tag{26}$$

3. Negative ion formation

Two types of negative ion are formed, O_2^- and O^-. The molecular ion is formed with electrons of low kinetic energy. The atomic ions result from collisions between molecules and electrons of sufficient energy to disrupt the molecule. This emerges from the studies of Bradbury,[40] Loeb,[41] Block and Bradbury[42] and

[35] L. B. Loeb, Phys. Rev. **17**, 89 (1921).
[36] N. Bradbury and E. Tatel, J. Chem. Phys. **2**, 836 (1934).
[37] S. C. Lind, reference 10, p. 153.
[38] H. D. Smyth, Proc. Roy. Soc. **A105**, 116 (1924).
[39] J. Tate and P. Smith, Phys. Rev. **39**, 270 (1932).
[40] N. Bradbury, Phys. Rev. **44**, 883 (1933).
[41] L. Loeb, Phys. Rev. **48**, 684 (1935).
[42] F. Bloch and N. Bradbury, Phys. Rev. **48**, 689 (1935).

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Lozier.[20] According to Lozier, there are two types of dissociation yielding atomic negative ions:

$$O_2+\epsilon=O+O^- -2.9 \text{ ev} \quad (27)$$

$$O_2+\epsilon=O'+O^- -12.0 \text{ ev}. \quad (28)$$

The electron affinity of molecular oxygen is estimated by Loeb to be less than 0.34 ev, while Block and Bradbury set the limits between 0.07 and 0.19 ev. It is sufficiently small that the electron can be removed from the molecule ion in neutralization processes at distances from the positive ion so large that the residual O_2 molecule is not affected.

4. The total processes and chemical reactions

The energy of the alpha-particle is sufficient to form one positive ion, O_2^+ or O^+, and, in addition, to break up another molecule to form a negative ion and an atom or two neutral atoms. In case the electron uses up its energy in excitation processes it can finally attach itself to an oxygen molecule to form O_2^-. All the neutralization processes possible lead to the same products, four oxygen atoms per ion pair, some normal and others excited

$$2O_2+\alpha\rightarrow 4O. \quad (29)$$

On the basis of the photochemical ozone yield of 1.3–2 molecules per quantum, the maximum ozone yield in the alpha-particle reaction should lie between 2.6 and 4. The experimental values average 1.7, with Lind reporting two results greater than 2. It is evident that the reverse deozonization reaction reduces the experimental yield below the maximum theoretical yield, as is further evident from the minimal ion yields of ozone in static systems. The maximum oxygen atom yield in the process assumes importance in the alpha-particle oxidation now to be considered.

IV. Radiochemical Reactions in Carbon Monoxide-Oxygen Mixtures

In a mixture of gases the energy of the alpha-particle is used by the different species according to the specific stopping power, S_i, the specific ionization, I_i, and the partial pressure, p_i. If N_{CO} is the number of ions produced in carbon monoxide and N_{O_2} the number in oxygen, then

$$N_{CO}/N_{O_2}=S_{CO}I_{CO}p_{CO}/S_{O_2}I_{O_2}p_{O_2}.$$

According to Lind, $S_{CO}I_{CO}=100$ and $S_{O_2}I_{O_2}=110$ so that, to a good approximation, the ratio of ions produced and energy consumed in the two gases respectively is proportional to the partial pressures. To the approximation to which the law of mixtures for ionization is valid, the ratio of the energy consumed by the various components will be equal to the ratio of the number of ions formed in each. Thus, we obtain, from the data in Sections I and III, the following yield per ion pair in a mixture of the gases before neutralizations set in:

$$\frac{p_{CO}}{p_{CO}+p_{O_2}}[(1-w)CO^++wC^++C+O+wCO_2]$$
$$+\frac{p_{O_2}}{p_{CO}+p_{O_2}}[aO_2^++bO^++cO+dO^-+fO_2^-], \quad (30)$$

where $0.5a+b+c+d=4$. Since all neutralizations now involve at least two atoms, we expect, on neutralization of charges:

$$\frac{p_{CO}}{p_{CO}+p_{O_2}}[2C+(2-w)O+wCO_2]$$
$$+\frac{p_{O_2}}{p_{CO}+p_{O_2}}[4O]. \quad (31)$$

Since each atom of oxygen will eventually oxidize one molecule of carbon monoxide to dioxide (see Eqs. (21) and (22)), and since, under the experimental conditions, with oxygen and carbon dioxide present, each carbon atom finally produces a carbon dioxide molecule:

$$C+CO=C_2O$$
$$C_2O+O_2=CO_2+CO$$

or, in sum,

$$C+O_2=CO_2,$$

it follows that the yield from the species present in *either* of the two square brackets in (31) will be exactly four molecules of carbon dioxide. Therefore, the ion pair yield will be $4CO_2$ independent of the concentrations of carbon monoxide or oxygen. This result is in exact agreement with the experimental result of Lind and Bardwell. The more recent value of Lind and Rosen-

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blum which yielded $2.5CO_2$ per ion pair was based on a calculation including ions produced not only from the reactants, but also those from the carbon dioxide product, the latter with an assumed fractional efficiency (see Section V). We have had access to some recalculations of the data by Rosenblum which reveal that all the experiments are in best agreement with the result deduced above, that the carbon dioxide yield is $4CO_2$ per ion pair produced from the carbon monoxide and oxygen present. The work of Brewer and Kueck,[43] in which carbon monoxide was oxidized in a glow discharge, showed that the yield per ion pair was about two molecules of carbon dioxide. In agreement with Gunther,[8] and with Lunt,[44] we emphasize the difficulties involved in this technique and expect therefrom only the order of magnitude of the yield.

V. The Effect of Carbon Dioxide on the Oxidation Yield

The energy used in pure carbon dioxide per ion pair formed has been shown to result in the break-up of two molecules of carbon dioxide and the production, after neutralization, of

$$(2-p)CO+(2+p)O+pC,$$

where p is the fraction of the carbon dioxide ionized to yield CO^+ and $1-p$ is the fractional yield of CO_2^+. Each oxygen atom and each carbon atom ultimately converts one molecule of carbon monoxide into dioxide. There are thus produced $2+2p$ molecules of dioxide or $2p$ molecules per ion pair in excess of those which disappear in the ionization process. If p had a value of unity, the yield from carbon dioxide would be $2CO_2$ per ion pair or 50 percent of the yield of four obtaining in carbon monoxide-oxygen mixtures free from carbon dioxide. Experimentally, Lind and Rosenblum[12] found that the ionization in carbon dioxide was approximately 15 percent as efficient as that in the carbon monoxide-oxygen mixtures. This figure points to a value of $p=0.3(2p/4\times100=15)$. A low value of p such as this is very reasonable since, in the studies of electric discharge through carbon dioxide at low pressures and moderate voltages, the yield of CO^+ was approximately one-fifth that of CO_2^+, or a value of $p=0.17$. Alternatively expressed, a ratio of 5 : 1 in ionization to yield CO_2^+ and CO^+ indicates an efficiency of ionization for carbon dioxide, expressed on the Lind-Rosenblum basis, of 8.3 percent. Further, the exchange reaction already discussed, $CO_2^+ + CO = CO^+ + CO_2$, would tend to raise the efficiency of the carbon dioxide added over and above that calculable from its own primary ionization products. Calculations carried out by Dr. C. Rosenblum, with the available measurements, to determine a definitive value of p on the basis of the present method of treatment revealed that the precision of the experimental data was not adequate to assign a reliable value for the quantity p. The ionization products of carbon dioxide indicate quite definitely, if qualitatively, that the addition of this gas to carbon monoxide-oxygen mixtures can only exercise a minor influence on the velocity of oxidation under the influence of alpha-particles.

VI. The Effect of Added Nitrogen on the Oxidation Yield

The ionization processes in nitrogen were reviewed by Smyth[18] and there is recent work by Tate, Smith and Vaughan.[45] Two processes occur:

$$N_2 = N_2^+ + \epsilon - 15.65 \text{ ev}$$

and

$$N_2 = N^+ + N + \epsilon - 24 \text{ ev}.$$

At 100 ev the ratio of N_2^+ to N^+ is about 10 : 1. These later workers observed no negative ion formation but Smyth and Hogness and Lunn[46] observed minute traces of N_2^-. Bradbury considers negative ion formation in nitrogen very improbable.

The excitation processes in nitrogen have been abundantly studied.[47] As is well known, in discharge tubes, active nitrogen is formed, known to be chemically very reactive, and containing both nitrogen atoms and excited metastable nitrogen molecules.[48] Three-body recombination

[43] K. Brewer and P. D. Kueck, J. Phys. Chem. **35**, 1281 (1931).
[44] R. W. Lunt, Trans. Faraday Soc. **32**, 1691 (1936).
[45] J. T. Tate, P. Smith and A. Vaughan, Phys. Rev. **48**, 525 (1935).
[46] Hogness and Lunn, Phys. Rev. **26**, 786 (1925).
[47] See H. Sponer, *Molekülspektren*, Vol. II (Julius Springer, Berlin, 1936), p. 458.
[48] Cario, Zeits. f. Physik **89**, 523 (1934).

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of nitrogen atoms may occur:

$$N+N+M=N_2+M+7.35 \text{ ev.}$$

The metastable molecules have 6.14 ev energy of excitation, and active nitrogen is known to react with oxygen.[49] Further, there is the possibility of exchanges in ionization such as:

$$N_2^+ + CO = CO^+ + N_2 + 2.15 \text{ ev,}$$

which may contribute to the initiation of the oxidation reactions. In a complex of products from an ionization process such as this it is obviously impossible to subject the system to a quantitative treatment. It is, however, quite evident that the addition of nitrogen to the carbon monoxide-oxygen system cannot fail to influence the velocity of the process as was actually found by Rosenblum.

[49] Wansborough-Jones, Proc. Roy. Soc. **A127**, 511 (1930).

The present analysis abundantly supports the point of view put forward by Eyring, Hirschfelder and Taylor in the ortho-parahydrogen conversion and the synthesis of hydrogen bromide as an explanation of alpha-particle reactions alternative to the older "cluster-theory." The preceding data indicate that the alternative is equally applicable to typical processes of alpha-particle decompositions, ozonization and oxidation processes. With increasingly available data on the primary products of ionization processes it may lead to satisfactory interpretation of all such processes.

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Slow Electron Scattering and the Apparent Electron Affinity of Mercury

J. H. SIMONS AND R. P. SEWARD
Department of Chemistry, Pennsylvania State College, State College, Pennsylvania
(Received July 28, 1938)

The scattering of slow electrons by gaseous molecules is discussed with the object of explaining the curves obtained when the apparent scattering area is plotted against a function of the electron velocity. The peaks frequently observed at about the ionization potential for most substances and the abnormally high values for the alkali metals are explained as being due to the formation or presence of positive ions. The rise in the curves for some substances, as the accelerating potential is diminished below the ionization potential, is explained as the result of an attractive force between the electron and the neutral molecule. It is shown that this attractive force for mercury approximates an inverse fourth-power law. From this law and an assumption of the diameter of the negative mercury ion, a reasonable value for the apparent electron affinity of mercury is calculated.

THE scattering of slow electrons in gases at low pressure has been studied by several investigators whose experiments have been summarized by Brode.[1] The effects are usually expressed in terms of α, the apparent cross section for scattering in square centimeters per cubic centimeter at 1 mm pressure and 0°C. Curves showing how α varies with the electron velocity show three distinct types. For argon, methane, etc., α is small for very slow electrons, increases to a maximum, and then decreases gradually as the electron speed increases. In some cases two or more maxima appear. For the alkali metals α at all electron speeds has a much greater value, and maxima and minima appear at lower electron velocities. Curves for the variation of α in zinc, cadmium, and mercury vapors show a very high value at the lowest electron speeds studied, a rapid falling off at higher velocities, and followed

[1] Brode, Rev. Mod. Phys. 5, 257 (1933).

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