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Silent Discharge Reactions in Aqueous Solutions. V. Nitrogen Fixation in a Heterogeneous System of Nitrogen and Water

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Nitrogen fixation by silent discharge on heterogeneous systems of nitrogen or air and water has been investigated, together with that on homogeneous systems of nitrogen or air. Moreover, oxidations of ferrous ions in acidic aqueous solutions of ferrous ions and in a ferrous-cupric ion system have been pursued in a nitrogen atmosphere. These experiments were conducted under flowing gas conditions. It has been found in the present study that: (1) in heterogeneous systems of nitrogen or air and water, the fixation yield is much larger in water than in gas; (2) in homogeneous systems of moist nitrogen or air, the yield is very small; (3) the ferric ion yield is very small compared with that expected theoretically from the estimated values of the absorbed dose ($\approx 3.2\times 10^7$ R/hr) and the LET (≈ 8 eV/Å), and (4) the effect of cupric ions on the ferric ion yield is negligible. Based on these findings, and in view of the actions of active nitrogen on radicals produced from water by slow electrons, the reaction mechanisms of nitrogen fixation have been suggested.

In this series of reports,[1,2] it has been reiterated that silent discharge reactions in an inert gas atmosphere can well be interpreted in terms of the radiolysis of water by slow electrons, and that they seem to correspond to the radiolysis caused by a particle of high LET (linear energy transfer).

Further, a precise study was made in the case of gases other than inert gases, such as hydrogen.[3] The process accompanying the action of active species of hydrogen was very complex, but it could be well explained by considering the scavenging action of the active species of hydrogen on the hydroxyl radical and on the hydrogen atom formed from liquid water by slow electrons.

In this study, nitrogen gas was used as the atmosphere, and the effect on the aqueous solutions of the active nitrogen generated in the gas phase was investigated.

During the progress of this study, it was found that a large amount of nitrogen was fixed in the water of a heterogeneous system of nitrogen and water.

Many studies of nitrogen fixation have been made in the fields of electric discharge and radiation chemistry.[4-7] It appears, however, that the importance of liquid water in the process of nitrogen fixation has not been adequately explored.

In order to elucidate the role of liquid water in nitrogen fixation, the gas-phase reactions of homogeneous systems of moist air or nitrogen have been studied.

The reactions of acidic aqueous solutions of ferrous ions and of a ferrous-cupric ion system in a nitrogen atmosphere have also been studied.

The reaction mechanisms of nitrogen fixation, though complicated, could be well interpreted by considering the action of the active nitrogen generated in the gas phase on the radicals formed from liquid water by slow electrons, in the same manner as in a hydrogen atmosphere.

Experimental

The discharge tube, the electrical circuit, and the experimental conditions employed were identical with those previously reported.

The flow velocity of the gases was about 120 m*l*/min. A constant electric discharge current of 1 mA was employed in all the experiments.

The experiments were all conducted at a constant solution volume of 10 m*l* and at a room temperature of about 20°C, after the oxygen dissolved in the solution had been removed by bubbling nitrogen gas into the solution.

Dry air or mosit air and moist nitrogen were prepared by passing each gas through phosphorus pentoxide or into the water of a washing bottle (see C of Fig. 1).

The amounts of nitrogen fixed in the gas phase were determined as nitrate, nitrite, and ammonium ions formed by passing the discharged gas into the water of an absorption bottle (B of Fig. 1).

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[1] Parts I and II of this series: A. Yokohata and S. Tsuda, This Bulletin, **39**, 46, 53 (1966).

[2] Part IV of this series: A. Yokohata and S. Tsuda, *ibid.*, **40**, 294 (1967).

[3] Part III of this series: A. Yokohata and S. Tsuda, *ibid.*, **39**, 1636 (1966).

[4] O. R. Wulf and E. J. Jones, *Phys. Rev.*, **37**, 471 (1931).

[5] R. N. Varney, *J. Chem. Phys.*, **23**, 866 (1955); *Phys. Rev.*, **79**, 708 (1957).

[6] P. Harteck and S. Dondes, *J. Chem. Phys.*, **27**, 546 (1957); **28**, 975 (1958); *J. Phys. Chem.*, **63**, 956 (1959).

[7] A. R. Jones, *Radiation Res.*, **10**, 655 (1959).

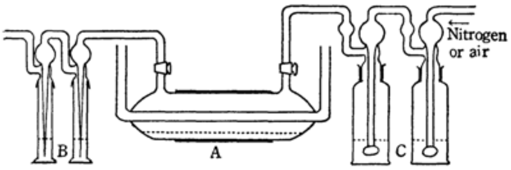

Fig. 1. Electrical discharge assembly.
—— Tin foil ---- Surface of solution

Analysis. Nitrite ions were determined by the colorimetric method,[8] while nitrate ions were determined as were nitrite ions but by zinc reduction. The analysis for ammonium ions was carried out by the use of Nessler's reagent. Hydrazine and hydrogen peroxide were determined colorimetrically by the reagents of *p*-dimethylaminobenzaldehyde[8] and titanic acid[9] respectively. The ferric ions produced were measured directly as a sulfate complex at 304 mμ.

Materials. Triply-distilled water was used in all the runs. As pure nitrogen gas (>99.95%) provided the same results as purified nitrogen gas,[10] it was used without further purification in later experiments. Reagent-grade sulfuric acid, ferrous sulfate, and cupric sulfate were also used without further treatment.

Results

As a typical example of the relationship between the applied voltage and the electric current, Fig. 2 shows the results obtained in the heterogeneous system of nitrogen and water, where F is the firing voltage.

Table 1 summarizes the firing voltages and the applied voltages under a constant current of 1 mA.

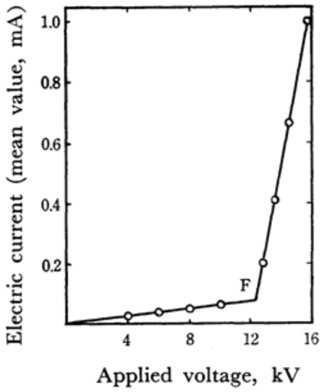

Fig. 2. Relation between applied voltage and electric current.

TABLE 1. THE FIRING VOLTAGES AND THE APPLIED VOLTAGES UNDER THE CONSTANT CURRENT OF 1 mA

Discharge system	Firing voltage kV	Applied voltage kV
Dry nitrogen	15	18
Moist nitrogen	15	18
Nitrogen+Water	12	16
Dry air	14	18
Moist air	14	18
Air+Water	12	16

TABLE 2. AMOUNT OF NITROGEN FIXED IN THE GAS PHASE

(discharge current: 1 mA,
duration of discharge: 10 min)

Gas	Nitrate ions formed in B of Fig. 1 10^{-4} mol/l	Nitrite ions formed in B of Fig. 1 10^{-4} mol/l
Moist nitrogen	2.9	1.1
Moist air	1.2	0.1
Dry air	35.6	0.1

TABLE 3. AMOUNT OF NITROGEN FIXED IN THE HETEROGENEOUS SYSTEM OF NITROGEN OR AIR AND WATER

(discharge current: 1 mA,
duration of discharge: 10 min)

Atmosphere	Products found in A of Fig. 1 10^{-4} mol/l			
	NO_3^-	NO_2^-	NH_4^+	N_2H_4
Nitrogen	60	11	9.0	trace
Air	82	1	0	0

Atmosphere	Products found in B of Fig. 1 10^{-4} mol/l			
	NO_3^-	NO_2^-	NH_4^+	N_2H_4
Nitrogen	3.0	0.9	0.4	0
Air	0.5	trace	0	0

The values of the dissipated energy, as calculated by applying these values to Eq. (2), were almost identical in all the discharge systems.

The results of nitrogen fixation are summarized in Tables 2 and 3. It has been found that: (1) in the case of air, the fixation of nitrogen is strongly suppressed by the presence of water vapor; (2) no significant difference between the amount of nitrogen fixed in moist nitrogen and that in moist air can be observed; (3) in a heterogeneous system of nitrogen or air and water, a larger quantity of nitrate ions is found in water than in mosit nitrogen or air, together with relatively small quantities of nitrite and ammonium ions, and so the amount of nitrogen fixed in water is almost

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[8] T. Rigg, G. Scholes and J. Weiss, *J. Chem. Soc.*, **1952**, 3034.

[9] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis II," D. Van. Nostrand Company, New York (1949), p. 882.

[10] R. Fricke and J. Kubach, *Z. Electrochem.*, **53**, 76 (1949).

the same when either air or nitrogen is used as the atmosphere.

Figure 3 shows the relationship between the duration of discharge and the quantity of nitrate ions formed in the water of the heterogeneous systems of nitrogen-water and air-water, while Fig. 4 shows the relationship between the duration of discharge and the quantity of nitrite ions. The relation between the yields of nitrate ions and nitrite ions and the duration of discharge was found to be linear, except in the case of nitrite ions formed in the air-water system.

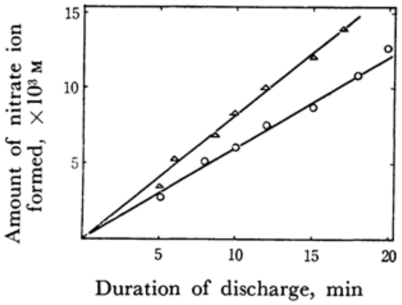

Fig. 3. Relationship between amount of nitrate ion formed and duration of discharge.
○ Nitrogen-water △ Air-water

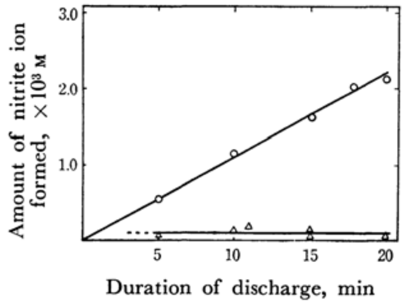

Fig. 4. Relationship between amount of nitrite ion formed and duration of discharge.
○ Nitrogen-water △ Air-water

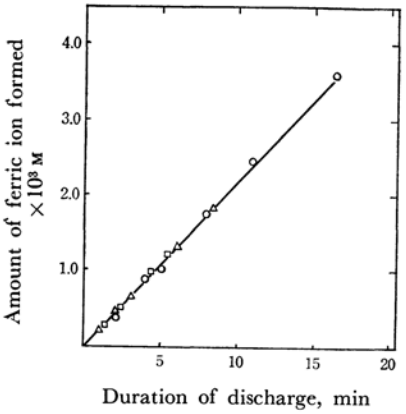

Fig. 5. Relationship between amount of ferric ion formed and duration of discharge.
△ 2×10^{-3} M $FeSO_4$ ○ 5×10^{-3} M $FeSO_4$
□ 2×10^{-3} M $FeSO_4$ + 2×10^{-2} M $CuSO_4$
H_2SO_4: 0.4N

Moreover, to obtain more information on the reaction mechanism of nitrogen fixation, studies were made on acidic aqueous solutions of ferrous sulfate and on those of a mixed system of ferrous sulfate-cupric sulfate in a nitrogen atmosphere. As is shown in Fig. 5, ferrous ions were oxidized to ferric ions. The yield of ferric ions was independent of the concentration of ferrous ions in the range from 5×10^{-3} M to 2×10^{-3} M and showed a good linear correlation with the duration of discharge. The effect of cupric ions added to make the concentration ratio of cupric ions to ferrous ions 10 : 1, was not appreciable within the range of experimental error. This finding is noteworthy, being contrary to the result obtained in inert gases. It suggests that the number of hydrogen atoms to be scavenged by cupric ions is very small.

Although hydrazine was also found, its yield was negligibly small when compared with those of the other products. Moreover, in a nitrogen atmosphere, contrary to expectation, hardly any hydrogen peroxide was found in water in either the A or B part of Fig. 1.

TABLE 4. CALCULATED RATIO OF $A(N_2)$ TO A(He)

V_d/V_i	$A(N_2)/A(\mathrm{He})$
0.2	8.6
0.4	8.2

Discussion

The Estimation of the Absorbed Dose in Aqueous Solutions. It has been pointed out in previous reports that, in silent discharge in an inert gas atmosphere, the absorbed dose can be estimated by chemical dosimetry. Furthermore, it has been shown that Eq. (1) held good:

$$A(\mathrm{He})/A(\mathrm{Ar}) = E(\mathrm{He})/E(\mathrm{Ar}) \tag{1}$$

where A is the value calculated by Eq. (2)[11] from the standpoint of electrical engineering and gives the total energy dissipated per second by the silent discharge, and where E is the dose absorbed in the solution per second.

$$A = \frac{f(C_{die}+C_a)(V_i+V_d)\{2E_m-(V_i+V_d)(1+C_a/C_{die})\}}{1+C_a/C_{die}} \tag{2}$$[12]

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[11] S. Fuji and N. Takimura, *Bulletin of the Electrotechnical Laboratory (Denki Shikensho Hokoku)*, **16**, 837 (1952).

[12] where,
f: the frequency of the electric source used
C_{die}: the total capacitance of the insulator
C_a: the capacitance due to the gap space in the tube
V_i: the voltage across the gap space at the firing voltage
V_d: the stopping voltage
E_m: the maximum value of the applied voltage

The validity of applying Eq. (1) to other gases has already been pointed out. Therefore, Eq. (3) can be obtained:

$$A(N_2)/A(X) \simeq E(N_2)/E(X) \qquad (3)$$

where X is helium or argon. Since $A(N_2)$ and $A(X)$ can be calculated by Eq. (2) and since $E(X)$ is known, $E(N_2)$ can be determined from Eq. (3).

Under our experimental conditions, $C_{die}=180\text{p}F$, $C_a=36\text{p}F$, $V_i=1.3$ kV, and $E_m=15.4$ kV in helium, while $V_i=12.2$ kV and $E_m=23.6$ kV in nitrogen. By applying these values to Eq. (2), the ratio of the dissipated energy in helium and nitrogen can be estimated. Table 4 shows the calculated results when $V_d/V_i=0.2$ and 0.4. In this study the mean value for $A(N_2)/A(\text{He})$ was estimated to be about 8.4. As $E(\text{He})$ is equal to 3.8×10^6 R/hr, $E(N_2)$ can be estimated to be about 3.2×10^7 R/hr. This value, of course, varies with the value of the electric discharge current. Shown here are values in the case of 1 mA. This also gives the average integral dose absorbed by the aqueous solution in the apparatus used by the authors, where the volume of the solution is 10 m*l*.

An Estimation of the Apparent LET. In order to estimate theoretically the radical or molecular yield from the absorbed dose, it is necessary to ascertain the LET value of the electrons produced in the nitrogen atmosphere by silent discharge.(1)

In general, electrons in silent discharge at one atmospheric pressure have an energy distribution from just above zero to a value slightly higher than the ionization potential of the gas in which the discharge occurs.(13)

In view of the fact(14) that the ionization potential of a nitrogen molecule is 15.6 eV, that of argon, 15.7 eV, and that of helium, 24.5 eV, the LET value of electrons in a nitrogen atmosphere may closely resemble that in argon. Therefore, a value of about 8 (eV/Å) was assumed for the LET value of electrons in nitrogen. Accordingly, the *G* values can be assigned as follows:

$$G(\text{H})=0.7,\quad G(\text{OH})=0.7,\quad G(\text{H}_2\text{O}_2)=1.4,$$
$$\text{and}\quad G(\text{Fe}^{3+})=4.2$$

The Formation of Active Nitrogen in an Atmosphere. It is well known that some species of a high chemical reactivity can be produced by electric discharge in a nitrogen atmosphere.(15-17) Pshezhetsky,(18) in reviewing the formation of oxides of nitrogen, included other results as well as those of himself and his co-workers, obtained using both fast and slow electrons and gamma-rays. Confirming the early assumptions(19,20) that oxides of nitrogen appear at electron potentials where the ionization of nitrogen begins, he showed that nitrogen oxidation begins at 16 eV (N_2^+) and accelerates sharply at 24 eV (N^+). Dmitriev and Pshezhetsky(21) found the most important reaction of nitrogen fixation to be:

$$N_2^+ + O_2 \rightarrow NO^+ + NO \qquad (4)$$

$$N_2^+ + O_2 \rightarrow NO_2^+ + N \qquad (5)$$

$$N + O_2 \rightarrow NO + O \qquad (6)$$

$$N + O_2 + M \rightarrow NO_2 + M \qquad (7)$$

On the other hand, according to the results of a mass spectrometric study(22) the only constituent probably present in a measurable concentration in active nitrogen is atomic nitrogen in the normal ^4S electronic state. Besides the aforementioned nitrogen atoms and molecular ions, metastable atoms or molecules may also play some role as active nitrogen.(23,24)

The formation of active nitrogen in the atmosphere should be also expected in the present work. Though it is very important to clarify the state of active species, this study is concerned only with reactivity. The reactivity of this species will be discussed in relation to nitrogen fixation. "N_{act}" will be arbitrarily used as a symbol of the active species.

The Nitrogen-fixation Yield. The nitrate-ion yield decreased remarkably in moist air compared with dry air. Also, the yield in moist air was almost identical with that in moist nitrogen (Table 2).

In the field of radiation chemistry, Wright *et al.*(25) have already examined the production of nitric acid in the Harwell BEPO Reactor by enclosing samples of water and nitrogen (or air) in fused ampoules. The yield of nitrate ions in air-water systems was almost equivalent to that in nitrogen-water systems. From this agreement, an interesting conclusion was reached that the

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13) N. R. Dibelius, J. C. Fraser, M. Kawahata and C. D. Doyle, *Chem. Eng. Progress,* **60**, 41 (1964).

14) K. Watanabe, T. Nakayama and J. Mottl, *J. Quant. Spectr. Radiative Transfer,* **2**, 369 (1962).

15) R. J. Strutt, *Proc. Roy. Soc. (London,)* **A85**, 219 (1911).

16) Rayleigh, *Nature,* **114**, 717 (1924).

17) T. Mukaibo and Y. Arai, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 312 (1954).

18) S. Y. Pshezhetsky, *A. E. C. Translation,* **1**, 23 (1957).

19) O. H. Wansbrough-Jones, *Proc. Roy. Soc. (London)*, **127A**, 511 (1930).

20) L. A. M. Henry, *Bull. Soc. Chim. Belges.,* **40**, 371 (1931).

21) M. T. Dmitriev and S. Y. Pshezhetsky, *A. Energ.*, **3**, 350 (1957).

22) G. B. Kistiakowsky and G. G. Volpi, *J. Chem. Phys.,* **27**, 1141 (1957).

23) H. G. V. Evans and C. A. Winkler, *Can. J. Chem.,* **34**, 1217 (1956).

24) J. F. Noxon, *J. Chem. Phys.,* **36**, 926 (1962).

25) J. Wright, J. K. Linacre, W. R. March and T. H. Bates, *Gevena Conf.,* **7**, 560 (1955).

reaction of nitrogen in the gas phase is not with oxygen, but with water vapor.

Our results are qualitatively consistent with those of Wright *et al.* However, particular attention should be paid to the findings that, as is shown in Table 3, the amount of nitrogen fixed in the water present in the discharge tube is very large when compared with that in the gas phase. These findings suggest that both the oxygen and the hydrogen of the nitrogen compounds formed in the water of the discharge tube originate principally from water, not from water vapor.

The Oxidation of Ferrous Ions. In silent discharge, the mechanism of oxidizing ferrous ions to ferric ions in an acidic solution can be shown as follows:

$$OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \qquad (8)$$

$$H + H^+ + Fe^{2+} \rightarrow Fe^{3+} + H_2 \qquad (9)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH + OH^- \qquad (10)$$

The yield of ferric ions, $Y(Fe^{3+})$, should, then, be expressed by 11:

$$Y(Fe^{3+}) = 2Y(H_2O_2) + Y(H) + Y(OH) \qquad (11)$$

where Y is the yield of products when the discharge current is 1 mA and when the duration of discharge is 10 min.

The estimated yield of ferric ions, $Y_{cal}(Fe^{3+})$, calculated on the basis of the absorbed dose and the $G(Fe^{3+})$ value, should be about 2.2×10^{-2} M. However, the experimental results shown in Fig. 5 give the value of $Y(Fe^{3+})$ to be only 2×10^{-3} M. This great discrepancy suggests that only a small part of the yields of radicals and hydrogen peroxide to be expected theoretically from the radiolysis of water by slow electrons contributes to the oxidation of ferrous ions to ferric ions.

On the other hand, a previous study of a ferrous-cupric ion system in an inert gas atmosphere showed that the addition of cupric ions reduces the yield of ferric ions because the occurrence of reaction (12), which removes hydrogen atoms, is followed by the reduction of ferric ions *via* reaction (13):

$$Cu^{2+} + H \rightarrow Cu^+ + H^+ \qquad (12)$$

$$Fe^{3+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+} \qquad (13)$$

Therefore, $Y(Fe^{3+})$ is finally given as:

$$Y(Fe^{3+}) = 2Y(H_2O_2) + Y(OH) - Y(H) \qquad (14)$$

In this work, however, hardly any effect of additive cupric ions has been found, suggesting that the hydrogen atom does not contribute to the oxidation of ferrous ions.

The Reaction Mechanism. The formation of nitrogen monoxide by the reaction of active nitrogen with active oxygen is well known in the field of electric discharge. The main reactions can be shown as follows:

$$N_2 \rightarrow N_{act} \text{ (active nitrogen)} \qquad (15)$$

$$O_2 \rightarrow O + O \qquad (16)$$

$$N_{act} + O \text{ (or } O_2,\ O_3) \rightarrow NO \qquad (17)$$

Since the production of the oxygen radical is strongly influenced by the presence of water vapor,[26] reaction (17) should be naturally suppressed. Thus, in moist air, the decrease in the precursor of the nitrate ion can be well interpreted in terms of the scavenging effect of water vapor on the oxygen radical.

Assuming that the main active species is the nitrogen ion, the charge transfer of the nitrogen ion to water vapor may be considered:[27]

$$N_2^+ \text{ (or } N^+) + H_2O \rightarrow N_2(N) + H_2O^+ \qquad (18)$$

However, this contribution to the suppression of nitrogen fixation has not yet been well established, and thus it is a problem for future study.

In the case of moist nitrogen also, the precursor of nitrate and nitrite ions is formed by silent discharge. This finding seems to suggest that nitrogen fixation arises from the reaction between nitrogen and water vapor. In this work, however, we wish to emphasize that this reaction mechanism can not be important, because the amount of nitrogen fixed in the atmosphere is very small when compared with the amount formed in the water present in the discharge tube.

Many of above-mentioned findings suggest that the hydrogen atoms, hydroxyl radicals, and hydrogen peroxides formed in water play an important role in nitrogen fixation.

The following reaction mechanism is tentatively proposed:

$$H_2O \text{ (liquid)} \xrightarrow{\text{slow electron}} H,\ OH,\ H_2\ H_2,O_2 \qquad (19)$$

$$N_{act} + H \rightarrow R \qquad (20)$$

$$N_{act} + OH \rightarrow S \qquad (21)$$

$$R,\ S \xrightarrow{\text{oxidation}} NO_2^-,\ NO_3^- \qquad (22)$$

$$R \xrightarrow{\text{reduction}} NH_4^+,\ N_2H_4 \qquad (23)$$

R and S are the reaction products (NH and NO are chiefly expected). The main oxidizing and reducing species might be hydroxyl radicals, hydrogen peroxides, and hydrogen atoms.

In an earlier study, reaction schemes of active species with radicals such as are shown in (20) and (21) were formulated for a hydrogen atmosphere and were found to be very useful in interpreting the experimental results.

Generally, in silent discharge radicals are formed mainly just below the water surface, because the energy of the electrons is very small. Accordingly,

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[26] E. J. Hellund, "The Plasma State," Reinhold Publishing Co., New York (1961), p. 81.

[27] A. Yokohata and S. Tsuda, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 689 (1965).

the occurrence of reactions (20) and (21) is very probable.

Lastly, it should be mentioned that the fixation yield is consistent, to some extent, with the yield of radicals expected theoretically.

It may be concluded that nitrogen fixation in a heterogeneous system of nitrogen and water can be well interpreted in terms of the action of active nitrogen generated in the gas phase on the radicals formed from liquid water by slow electrons in the *same manner as has been described* in our previous reports.