[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

THE NATURE OF ACTIVE NITROGEN: THE SYNTHESIS OF AMMONIA FROM THE ELEMENTS[1]

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The question concerning the nature of glowing active nitrogen has been a much discussed and controversial subject. It is unnecessary here to sketch historically the study of active nitrogen which has led to the atomic and molecular hypotheses of its nature[3] since this has been amply recorded in other works. Birge,[4] Sponer[5] and Birge and Sponer[6] have shown that the eleventh vibrational state of the 9.3-volt electron level, from which the strongest bands in the afterglow proceed, corresponds to 11.4 volts above the normal level and this represents the true energy of combination of nitrogen atoms. This checks with other evidence as discussed by Birge and Sponer[6] as well as with the extrapolated value of the first band in the Lyman-Birge-Hopfield band system formerly attributed to NO by Sponer[4b] but now known to belong to the nitrogen mole-

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[1] Read before the 74th Meeting of the American Chemical Society at Detroit, September 5–10, 1927.

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[3] It is very important to make clear the distinction between the atomic and molecular theories with respect to the formation of the afterglow. According to the former, the carriers issuing from the discharge are neutral, unexcited nitrogen atoms which potentially have it within their power to create the glow by means of an activating process involving, as far as our knowledge will allow us to judge, a triple collision between two N atoms and a N_2 molecule. An uncertainty exists regarding the necessity for a triple collision because, unlike the H_2 molecule, the N_2 molecule has definite and known quantized states from which it can radiate, corresponding to the energy of dissociation plus the relative kinetic energy of the atoms. While a three body collision in the case of the combination of H atoms is an absolute necessity, since there is no molecular quantum state here from which radiation is possible, yet in the N_2 molecule it is possible that two N atoms may combine without the presence of a third body. There are certain difficulties confronting the assumption of a three body collision in active nitrogen (see Bonhoeffer and Kaminsky[8]). It is hoped to treat this in a forthcoming publication. At any rate an excited N_2 molecule results (probably unstable) which gives rise to emission of the afterglow; the α-bands are emitted by transition from vibrational states in level B to several vibration states in level A (see Birge and Sponer[6]), those probably being meta stable. According to the molecular theory the activating process does not occur outside the discharge, since the carriers are held to be metastable excited molecules which originate in the discharge. These have a long life and eventually emit radiation. In the atom theory excitation of metal atoms (Hg, etc.) occurs either by a triple collision with N atoms or by a collision with the resulting excited N_2 molecule. In the molecular theory this excitation takes place directly by collisions with excited N_2 molecules.

[4] (a) Birge, *Nature*, **114**, 642 (1924); (b) **117**, 81 (1926).

[5] Sponer, *Z. Physik*, **34**, 622 (1925).

[6] Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926).

cule.[7] Furthermore, a study[8] of the dependence of the afterglow intensity on the concentration of the active constituent at constant total nitrogen pressure reveals that the relation is bimolecular in character. This and other evidence points strongly to the atom theory. The results of Willey and Rideal,[9] while correct as far as they go, cannot be taken to mean that active nitrogen is composed only of 2-volt excited molecules. These authors neglect to consider many reactions initiated by active nitrogen which require much more energy than 2 volts. The varied phenomena caused by active nitrogen make it evident that 2-volt level nitrogen molecules do not issue from the discharge. It is rather more probable that these vibrational states in the normal electron level, which in all probability are truly metastable, are brought into existence by collisions of the second kind between an ordinary nitrogen molecule and an excited nitrogen molecule in level B. The former takes up from 1 to $3^1/_2$ volts and the latter drops to level A. Vibrating molecules in the normal electron level may also be brought about by a jump from some higher electron level. We can attribute Willey and Rideal's results to molecules in these low vibrational states. In a recent work Constantinides[10] concludes that active nitrogen is an excited molecule having a metastable state between 9.4 and 10.4 volts. This is at variance with our knowledge concerning the origin of the first positive bands as mentioned above. This work will be discussed briefly in a later section.

The importance of determining whether active nitrogen contains atomic nitrogen is evident. The present experiments were undertaken with this in mind and they probably furnish the first kinetic evidence of its kind that nitrogen atoms are present in active nitrogen. In principle the experiments depend upon the formation of ammonia from the elements. It is easily shown that if unactivated nitrogen gas is mixed with atomic hydrogen (prepared by Wood's method), at least four successive and selective collisions passing through intermediate unstable compounds are necessary in order to form ammonia. The following set of equations is not intended to indicate the order of the steps involved nor the possibility of their occurrence, only that such a sequence is required to reach the final product.

$$N_2 + H = N_2H \qquad (1)$$
$$N_2H + H = N_2H_2 \qquad (2)$$
$$N_2H_2 + H_2 = N_2H_4 \qquad (3)$$
$$N_2H_4 + H_2 = N_2H_6 \longrightarrow 2NH_3 \qquad (4)$$

If the gases are brought together at low pressures the chance is very small that the entire series will be completed especially in view of the

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[7] Sponer, *Z. Physik*, **41**, 611 (1927).

[8] Bonhoeffer and Kaminsky, *Z. physik. Chem.*, **127**, 385 (1927).

[9] Willey and Rideal, *J. Chem. Soc.*, 1804, 1926; 669, 1927.

[10] Constantinides, *Phys. Rev.*, **30**, 95 (1927).

rarity of such encounters as depicted by Equation 2. Similarly it can be shown that on bringing together unactivated hydrogen and active nitrogen three or four successive and selective encounters are required, depending on whether the series commences with molecular or atomic nitrogen. In both of these types of experiments the chance for forming ammonia should be very slight. If now atomic hydrogen is mixed with active nitrogen there are two possibilities; with the metastable nitrogen molecule the sequence is composed of four steps similar to that given above; on the other hand if atomic nitrogen is present, only two steps are necessary, neither of them being of rare occurrence, since Wood's hydrogen contains a considerable amount of atomic hydrogen.

$$N + H = NH \quad (1)$$

$$NH + H_2 = NH_3 \quad (2)$$

Thus the synthesis of ammonia has the best chance of occurring, if at all, only when both gases are activated and provided the activated nitrogen contains atomic nitrogen. The alternative to such a series of steps would necessitate a triple, quadruple or quintuple collision which would still place the last-mentioned possibility in the most favorable position for ammonia formation. Of course, the presence of neutral, tri-atomic hydrogen might form ammonia in a single step, but its existence is extremely doubtful.[11]

There is one other possibility to be considered, namely, the following reaction with excited nitrogen molecules.

$$N_2' + H = NH + N \quad (1)$$

$$NH + H_2 = NH_3 \quad (2)$$

If this were taking place Caress and Rideal[12] would have observed ammonia formation in the gas phase at potentials corresponding to the numerous vibrational states in the 7.9-volt and 9.3-volt electron levels in the nitrogen molecule. Instead they found ammonia formation beginning at 13 volts, which they represented as a series of steps commencing with ordinary nitrogen and an excited H'_{13v}. Since their electron tube was not calibrated and a tungsten filament was employed, this voltage may be in error by at least one volt. While the hydrogen atom has critical potentials from 10.2 volts and up, it is strange why, if their mechanism is correct, ammonia is not formed in the gas phase at 10.2 volts, the first resonance potential of the hydrogen atom. Now this is very significant in view of the fact that level C (see Birge and Sponer[6]) of the nitrogen molecule begins at 13 volts and that the vibrational states of level B beginning at 9.3

[11] (a) Paneth, Klever and Peters, *Z. Elektrochem.*, **33**, 102 (1927); (b) Urey and Smallwood, unpublished material; (c) Bach, *Ber.*, **58B**, 1388 (1925); (d) Scanavy-Grigoriewa, *Z. anorg. allgem. Chem.*, **159**, 55 (1927); (e) Artius, *Dissertation*, Heidelberg, 1926; (f) Fischer and Iliovici, *Ber.*, **41**, 4452 (1908).

[12] Caress and Rideal, *Proc. Roy. Soc.* (*London*), **115**, 684 (1927).

volts extend up to about 12.8 volts. It is well known that in contradistinction to iodine and oxygen molecules, the nitrogen molecule does not dissociate in a primary act. According to Birge and Sponer in the case of certain excited electronic states (such as level B in nitrogen) dissociation does not take place when the energy of dissociation is reached even with collisions occurring. Assuming that one product of dissociation is an excited atom, their predicted break in the series of vibrational states to account for this is observed in C level, $n = 4$ at 13.94 volts. This may correspond to a collisional dissociation of the molecule into a normal nitrogen atom and a 2.5-volt excited N atom, which is possible from certain findings by Hopfield.[13] This is in agreement with conclusions derived from the extrapolated convergence limit of the upper band of the Lyman-Birge-Hopfield band system.[7] Thus Caress and Rideal's observed reaction in the gas phase at 13 volts ± 1 volt may, in the light of the foregoing, be represented more logically by excitation of the nitrogen molecule above its dissociation energy (probably to some vibrational state in the C level), followed by collisional dissociation into atoms. Ammonia is then easily formed through the medium of atoms as represented in a mechanism above.

Experimental

The electrodeless discharge for preparing active nitrogen, employed by other workers with excellent results, was substituted for the usual condensed discharge with internal electrodes, since the gas pressure was low. The experimental arrangement is shown in Fig. 1. The active nitrogen was prepared in a spherical bulb A (12.7 or 8.7 cm. in diameter) wound with a few turns of heavy copper wire. The electrical connections are evident. A zinc spark-gap was employed and the plate-glass lead foil condenser (5 in number, 18 × 20 inches) was immersed in transformer oil. The transformer primary was supplied with 9 to 10 amperes at 110 volts, 60 cycles, and the secondary voltage was about 20,000 volts. At a well-defined pressure (about 0.1 mm. in the 12.7 cm. and about 0.05 mm. in the 8.7 cm. bulb) a brilliant ring discharge appeared from which glowing active nitrogen was drawn and under good conditions could be observed to last between one and two minutes. Tank nitrogen was passed over heated copper to remove most of the oxygen, through soda lime and phosphorus pentoxide tubes and then through a liquid-air trap L, nearly atmospheric pressure being maintained by a mercury trap M. By means of a needle valve V, the pressure in A could easily be regulated at any desired value. Atomic hydrogen was prepared in a Wood's discharge tube B, 2 meters long and 2 cm. in diameter with cylindrical aluminum electrodes. The transformer primary was supplied with from 10–14.5 amperes at 110 volts, 60 cycles, and the secondary voltage was about 20,000 volts. The atomic hydrogen, whose presence could be shown by a glowing platinum strip, was drawn from the center of the discharge tube where the brilliant spectrum due to the Balmer series was always in evidence. The hydrogen was prepared from a potassium hydroxide solution in a long armed U-tube continuous generator G, care being taken to prevent the oxygen from mixing with the hydrogen by allowing the platinum electrodes to just touch the liquid surface in each arm. Any caustic in the gas was carefully removed. The pressure was regulated as

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[13] Hopfield, *Phys. Rev.*, 27, 801 (1926).

before by means of a needle valve. A calibrated McLeod gage was connected to both the nitrogen and hydrogen systems just before each gas entered its respective discharge tube. The entire apparatus with the exception of the needle valves was constructed of Pyrex glass. The gases, after leaving the discharge, were brought together in a chamber C, the hydrogen through a 1mm. nozzle about 24 cm. from its discharge tube and the nitrogen through a 2mm. stopcock about 20 cm. from the electrodeless discharge. The tubes leading from both discharges were grounded in several places with tin-foil to eliminate as far as possible stray high-frequency currents. Both transformers were at some distance from the discharges. A little excess pressure could be maintained on the hydrogen side. With due precaution exercised in starting an experiment, it was found that no mixing of the gases occurred outside the mixing chamber during the progress of a run. Any diffusion and mixing of the gases in either is immediately noticeable by suppression of the Balmer lines in the hydrogen tube and the appearance of a pinkish color instead of the usual greenish-yellow in the nitrogen discharge. All three types of experiments were carried out under the same conditions. Condensable gases were frozen out in a ground-glass jointed liquid-air trap D, the gases being pulled through the system by two high-vacuum oil pumps joined in parallel. At the close of an experiment the trap was removed, distilled water added while still in liquid air and the tube stoppered. Tests for ammonia were made with freshly prepared Nessler reagent and for hydrazine with selenious acid and silver nitrate, the hydrazine first having been stabilized with a drop of sulfuric acid. With selenious acid a reddish precipitate develops and with silver nitrate silver precipitates. Blank tests were made in every case with distilled water.

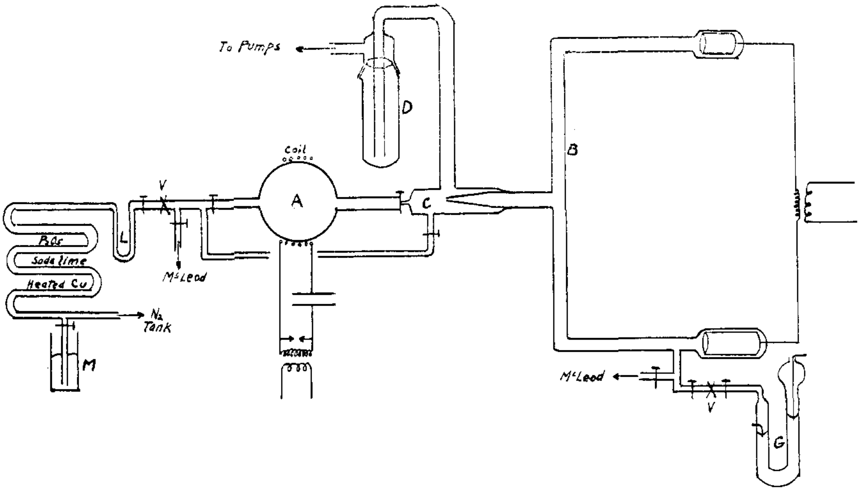

Fig. 1.

Results

The following table presents the results of a series of runs.

The results show that *ammonia is formed only when active nitrogen is mixed with atomic hydrogen.* From considerations presented above, this can be interpreted to indicate the presence of nitrogen atoms in active nitrogen.

TABLE I

RESULTS OF A SERIES OF RUNS

Press., mm. of Hg N_2	 H_2	Gas activated	Time of run, min.	Result and remarks
0.15	0.26	H_2	30	No NH_3. After one day no difference between test solution and blank test
.31	.42	H_2	60	No NH_3
.25	.375	H_2	60	No NH_3; no N_2H_4
.33	.38	H_2	85	No NH_3; no N_2H_4
.17	.28	H_2	60	No NH_3; no N_2H_4
.04	.10	H_2	60	No NH_3; no N_2H_4
.09	.15	N_2 and H_2	60	NH_3 present, deep yellowish-red characteristic color with $^1/_3$ of solution. No N_2H_4
.076	.076	N_2 and H_2	90	NH_3 present, deep characteristic color with $^1/_3$ solution. No N_2H_4
.04	.044	N_2 and H_2	85	NH_3 present; deep yellow color with tinge of red with $^1/_2$ of solution. No N_2H_4
.25	.39	Blank run, no activation	60	No NH_3; no N_2H_4
.045	.045	N_2	60	No NH_3; no N_2H_4
.047	.040	N_2	50	No NH_3; no N_2H_4

Discussion

To the author's knowledge this is the first attempt to bring together active nitrogen and atomic hydrogen after the activation of each gas separately. Previously either nitrogen or hydrogen alone or a mixture of the two gases was activated. The results of these experiments activating the nitrogen only are in agreement with those of other investigations.[14,9] *Active nitrogen has no effect on molecular hydrogen, no ammonia being formed.* The evidence for the formation of ammonia upon mixing ordinary nitrogen with atomic hydrogen is conflicting. Hirst[15] found ammonia and traces of hydrazine when hydrogen in the presence of nitrogen was activated by collision with optically excited mercury atoms. This may have been due to the presence of a mercury surface, which agrees with the observations of Caress and Rideal[12] on the formation of ammonia on a metal surface with hydrogen atoms and nitrogen molecules. At pressures above but not below atmospheric, W. A. Noyes, Jr.,[16] obtained ammonia at the temperature of boiling mercury by a similar method of hydrogen activation. On the other hand, H. S. Taylor,[17] employing the same means for excitation failed to detect any ammonia. Bon-

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[14] Strutt, *Proc. Roy. Soc.* (*London*), **85**, 219 (1911).

[15] Hirst, *Proc. Camb. Phil. Soc.*, **23**, 162 (1926).

[16] W. A. Noyes, Jr., THIS JOURNAL, **47**, 1003 (1925).

[17] (a) Taylor, *Trans. Faraday Soc.*, 21, 562 (1926); (b) THIS JOURNAL, **48**, 2840 (1926).

hoeffer[18] also failed to find ammonia using the Wood's discharge tube for producing atomic hydrogen. Cario and Franck[19] also obtained negative results with atomic hydrogen and molecular nitrogen. Willey and Rideal[20] state that they were able to obtain ammonia when a stream of nitrogen at 10 mm. pressure was led into a stream of hydrogen at a point 150 cm. (corrected by Dr. Willey) from a discharge tube through which hydrogen was flowing at the same pressure. The gas pressure was far too high for the preservation of atomic hydrogen 150 cm. from the discharge.[21] In Willey and Rideal's experiment the presence at the mixing point of any form of ionic hydrogen or an electronically excited atom is precluded and, since the existence of H_3 is problematic, it is a little difficult to understand what variety of active hydrogen they were dealing with. It may be concluded from the present results and other evidence available that *no ammonia is formed by atomic hydrogen and unexcited molecular nitrogen.*

In support of the present results on the formation of ammonia when both hydrogen and nitrogen were activated separately may be cited the experiments of Andersen[22] and Storch and Olsen[23] on the formation of ammonia from gaseous mixtures of nitrogen and hydrogen with slow electrons and in the low-voltage arc. Olsen[24] concludes that the main synthesis of ammonia is brought about by the presence of both normal nitrogen atoms and normal hydrogen atoms.

Brief mention should be made of Constantinides' experiments.[10] If the effects observed by him represent ionization, then it would appear that active nitrogen is able to ionize iodine but not mercury (ionization potentials, 9.4 volts and 10.4 volts, respectively). From this it was concluded "that active nitrogen is an excited molecule of nitrogen having a metastable state between 9.4 and 10.4 volts." This does not eliminate the atom theory as it would at first appear. Our knowledge of energy transfer in triple collisions is still obscure. Physical intuition would indicate that all the energy of combination of nitrogen atoms might not be transferred to systems like iodine or mercury, expecially in view of the known low vibration states in the normal electron level in the nitrogen molecule. This would be equally true whether these systems collided directly with two nitrogen atoms or with an excited nitrogen molecule. Furthermore, it is unreasonable to assume that a symmetrical collision between two nitrogen atoms and a nitrogen molecule would in-

[18] Bonhoeffer, *Z. physik. Chem.*, **119**, 385 (1926).

[19] Cario and Franck, *Z. Physik*, **37**, 619 (1926).

[20] Willey and Rideal, *J. Chem. Soc.*, 671, **1927**.

[21] Compare Kaplan, *Phys. Rev.*, **30**, 640 (1927).

[22] Andersen, *Z. Physik*, **10**, 54 (1922).

[23] Storch and Olsen, THIS JOURNAL, **45**, 1605 (1923).

[24] Olsen, *ibid.*, **48**, 1298 (1926).

volve the same energy transfer as a collision between two nitrogen atoms and iodine or mercury. This argument is very significant if the combination of nitrogen atoms involves a two body collision only. It is not at all surprising, therefore, to find that active nitrogen is incapable of transferring 10.4 volts to mercury. Active nitrogen even seems to be incapable of producing an active variety of hydrogen,[20] the dissociation of which requires only 4.2 volts. One prediction may possibly be allowable. The higher the nitrogen pressure the more readily are the α bands eliminated due to secondary collisions in which the excited nitrogen molecules are divested of small amounts of energy. This is borne out by observations on the afterglow decay time and intensity with increasing nitrogen pressure. At low pressures, therefore, active nitrogen may be expected to transfer more energy to mercury. Indeed, Ruark, Foote, Rudnick and Chenault,[25] by recording the emission of the mercury $2^3P_1 - 6^3D$ series at 0.02 mm. nitrogen pressure, showed that *at least* 10 volts could be transferred to mercury. It is possible that at this and lower pressures some mercury atoms may be ionized.

Conclusion

It may be concluded from these experiments that active nitrogen contains atomic nitrogen. Until the atomic origin of active nitrogen is shown definitely to be erroneous, this can be taken as supporting the present interpretation of spectroscopic data. Since the nitrogen molecule may exist in many states of excitation, it is evident that at any moment glowing active nitrogen would consist of a non-homogeneous mixture of normal nitrogen atoms and nitrogen molecules in a number of excited states. An intimation that active nitrogen contains more than one active constituent may be gathered from a conclusion of Lord Rayleigh (Strutt)[26] that "there does not appear to be any definite connection between the development of spectra by active nitrogen and the chemical actions in progress." Since this paper was originally written, a private communication from Dr. E. J. B. Willey and later his letter to *Nature*,[27] also a suggestion by Bonhoeffer and Kaminsky,[8] indicate that these workers also suspect the non-homogeneity of active nitrogen.

Summary

Experiments are described for determining whether atomic nitrogen is a constituent of glowing "active nitrogen." The latter, prepared at low pressures by an electrodeless discharge, was passed into a stream of atomic (Wood's) hydrogen. The resulting mixture yielded ammonia. Under the same conditions no ammonia was obtained when either the

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[25] Ruark, Foote, Rudnick and Chenault, *J. Optical Soc. Am.*, **14**, 17 (1927).

[26] Strutt, *Proc. Roy. Soc.* (*London*), **88**, 549 (1913).

[27] Willey, *Nature*, 119, 924 (1927).

nitrogen or hydrogen was activated alone. No hydrazine was found under any conditions. Considerations are presented showing that at low pressures ammonia would be expected, if at all, only when both the nitrogen and hydrogen are activated simultaneously and provided atomic nitrogen were present in the former. It is concluded that active nitrogen contains atomic nitrogen, which may be taken as support for the present interpretation of spectroscopic data. In addition it is concluded that glowing active nitrogen consists of a non-homogeneous mixture of nitrogen atoms and excited nitrogen molecules.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE SYSTEM WATER AND THE SULFATES OF SODIUM AND MAGNESIUM[1]

BY WALTER C. BLASDALE AND HOMER L. ROBSON

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In 1915 D'Ans[2] summarized the work of van't Hoff,[3] Roozeboom[4] and others on this system, and made sufficient new determinations to indicate the equilibrium relations in this system between 0 and 90°. The isotherm at 25° was determined by W. C. Blasdale in 1920 in connection with a study of the salt pair, sodium chloride—magnesium sulfate,[5] and the isotherm at 103° was similarly determined by Mayeda[6] in the same year. Archibald and Gale[7] in 1924 determined isotherms of this system at 0°, 10°, 18.7°, 25°, 30°, 40°, 50°, 60°, 80° and 100°, combining new determinations with the results of previous investigators. Their isotherms below 60° are in very fair agreement with those given by D'Ans, but those at 80 and 100° differ considerably. Mayeda's measurements disagree with those of D'Ans and of Archibald and Gale and are somewhat different from the values given in this paper.

The salts which occur below 60° are: the dodecahydrate, heptahydrate and hexahydrate of magnesium sulfate; sodium sulfate, decahydrate and

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[1] A part of this work was done under a grant made by the University of Saskatchewan from its research fund.

[2] D'Ans, *Kali*, 9, 177 (1915).

[3] Van't Hoff, *Rec. trav. chim.*, 6, 36 (1887); (b) van't Hoff and van Deventer, *Z. physik. Chem.*, 1, 170 (1887); (c) van't Hoff and Meyerhoffer, *Sitzb. preuss. Akad. Wiss.*, Berlin, **1904**, p. 1418; (d) van't Hoff, "Untersuchungen über der Bildungsverhaltnisse der Ozeanischen Salzablagerungen," 1912 ed., p. 281; (e) van't Hoff and O'Farrelly, *Sitzb. preuss. Akad. Wiss.*, Berlin, **1902**, p. 370; (f) "Untersuchungen," p. 198.

[4] (a) Roozeboom, *Rec. trav. chim.*, 6, 333 (1887); (b) Roozeboom, *Z. physik. Chem.*, 2, 513 (1888).

[5] Blasdale, *J. Ind. Eng. Chem.*, **12**, 164 (1920).

[6] Mayeda, *J. Chem. Ind. (Japan)*, **23**, 573 (1920).

[7] Archibald and Gale, THIS JOURNAL, **46**, 1760 (1924).