[Contribution from the Chemical Laboratory of the Johns Hopkins University]

# The Photochemical Reaction of Ammonia with Oxygen[1]

By H. E. Bacon and A. B. F. Duncan

Much information has been obtained in recent years about the action of light on gaseous ammonia. The ultraviolet absorption spectrum, first examined by Leifson,[2] has been reëxamined and analyzed by Dixon.[3] The decomposition of ammonia in monochromatic light has been studied by Warburg[4] and Kuhn.[5] Recently Kistiakowsky and Wiig[6] have confirmed the earlier results of Warburg, that the quantum yield in the reaction is 0.25. From the experiments of Bonhoeffer and Farkas[7] and from the diffuse character of the ultraviolet absorption bands, it must be concluded that absorption of light by ammonia results in dissociation without collision, the products being most probably $NH_2$ and H. On this basis Kistiakowsky and Wiig have suggested a mechanism to account for the low quantum yield in the decomposition of ammonia. It is of interest to study the oxidation of these primary products; accordingly, we have made observations, which are reported here, of ammonia–oxygen mixtures illuminated by light which the ammonia alone absorbs.

The reaction has been studied qualitatively by Berthelot and Gaudechon,[8] who exposed mixtures of ammonia and oxygen to the total radiation of the mercury arc. They found nitrogen, hydrogen and water as products, but neither nitrates nor nitrites. The present investigation shows that the reaction must be more complex than these workers supposed, since both nitrates and nitrites have been found.

## Experimental

**Purification of Gases.**—Commercial ammonia was distilled three times over potassium hydroxide pellets. Oxygen was prepared by heating pure barium peroxide in a quartz bulb to about 600°. A long tube of potassium hydroxide pellets was inserted to remove water and carbon dioxide. Tank hydrogen was passed through heated platinized asbestos, followed by a U-tube immersed in liquid air.

**Apparatus.**—The light source was a condensed spark between zinc electrodes. These were disks of chemically pure zinc[9] which revolved with equal speed at right angles to each other. The other parts were an 0.04 mfd. condenser across the gap, a 2.5 k.w. transformer drawing 17 amperes, and a small fan to keep the oxide from the optical system. A crystal quartz lens focused the light on the slit of a Bausch and Lomb quartz monochromator, or directly upon the reaction vessel. The monochromator slit was set at 2.5 mm. and the wave-length dial at 2050, after experiments had shown that maximum energy absorption resulted from this adjustment. Back of the monochromator exit slit a line thermopile was sealed in a glass case with a crystal quartz window, and was evacuated during use. Measurements of absolute energy later proved irrelevant, and further description is not justified.

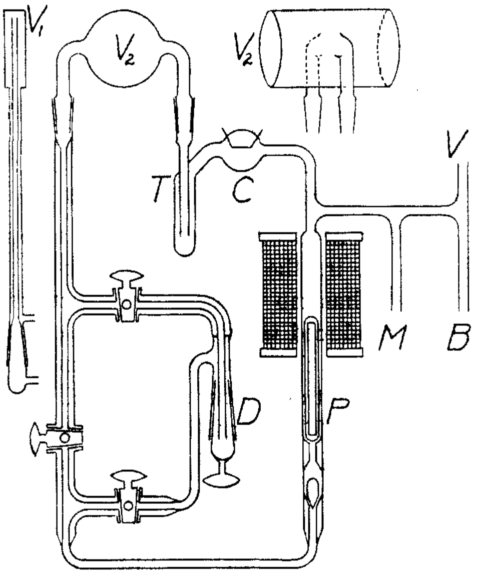

Fig. 1.—Reaction system.

In Fig. 1, $V_1$ and $V_2$ are two fused quartz reaction vessels which were used interchangeably; the distance between windows was 8 and 52 mm., respectively. A small inner tube allowed circulation in $V_1$. D is a drying trap, filled with freshly fused and powdered potassium hydroxide before each run, C a combustion bulb and T a trap. P is a magnetically operated, all glass circulating pump with a single valve; cylinder clearance allows the upward passage of gases. M is a constant volume capillary manometer, B a gas buret, and V leads to the vacuum system. All ground joints were sealed with piceïn. Except for rate measurements at short intervals, pressures were read with a cathetometer.

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[1] From a dissertation submitted by H. E. Bacon to the Board of University Studies of the Johns Hopkins University in partial fulfilment of the requirements for the Doctor of Philosophy Degree, October, 1933.

[2] Leifson, *Astrophys. J.*, **63**, 73 (1926).

[3] Dixon, *Phys. Rev.*, **43**, 711 (1933).

[4] E. Warburg, *Sitzb. preuss. Akad.*, **746** (1911); 216 (1912).

[5] W. Kuhn, *J. chim. phys.*, **23**, 521 (1926); *Compt. rend.*, **177**, 956 (1923).

[6] Kistiakowsky and Wiig, This Journal, **54**, 1806 (1932).

[7] Bonhoeffer and Farkas, *Z. physik. Chem.*, **134**, 337 (1928).

[8] Berthelot and Gaudechon, *Compt. rend.*, **150**, 1327 (1910).

[9] Furnished through the courtesy of the New Jersey Zinc Company.

**Measurements.**—Attempts were made to study the reaction in monochromatic light, following the ammonia pressure by freezing with liquid air and the energy absorption by thermopile readings. The available energy (about 1.41 × $10^{17}$ quanta per second) caused the ammonia pressure to decrease only about 5 mm. in 6 hours—subject to the error of small differences between large pressure readings. Other changes of equal magnitude, probably due to absorption, occurred without illumination. A final difficulty was the presence of liquid water, which prevented interpretation of pressure changes because of the solubility of ammonia.

It was expected that water would not condense until its pressure reached the saturation point of more than 20 mm. However, a liquid phase appeared much earlier in the form of fine droplets, which made a definite film on the quartz cell and left a white crystalline mass on evaporation. The deposit was absent from the illuminated area and formed on the window a sharp outline of the light path. Changes in the ammonia and oxygen concentrations, and in the energy absorbed, failed to prevent its appearance; and the absence of a sharp break in the pressure–time curve indicated that the liquid phase appeared early in the reaction. In total radiation the scattered light showed the light path to be filled with an unmistakable mist, which pulsated with the circulating pump; it disappeared when one of the reactants was exhausted, and the rapid drop in pressure which characterized the reaction was entirely absent as soon as the mist disappeared.

To avoid the difficulties mentioned, later experiments were conducted by analyzing the products of the reaction, and the total radiation of the zinc spark was used to obtain these in sufficient quantities for accuracy. Determinations of the quantum yield were based on experiments in which ammonia was decomposed under identical light conditions in the same vessel. The quantum yield of the decomposition was taken to be 0.25, as found by the investigators cited above.

Reference to the absorption spectrum of ammonia showed that of the total incident radiation only the lines at λ 2025, λ 2061.9, λ 2100 and λ 2138.5 were absorbed. The most intense line is close to the average wave length used, and from the standpoint of ammonia absorption it was felt that the zinc spark gave monochromatic light of wave length 2080 Å. *Qualitatively the reaction in strictly* monochromatic light was identified with that in total radiation by the similarity in the form of the curve, in the pressure change per quantum absorbed, and in the solid products determined by analysis.

TABLE I

| No. | Conditions | Initial $P_{NH_3}$ | Initial $P_{O_2}$ | Moles × $10^5$ $NH_3$ used | Moles × $10^5$ $O_2$ used | Moles × $10^5$ $N_2$ found | Moles × $10^5$ $H_2$ found | Moles × $10^5$ $NH_4NO_3$ found |
|---|---|---|---|---|---|---|---|---|
| | Small cell | | | | | | | |
| 18 | No circ. | 192.7 | 99.6 | 7.000 | 5.260 | 1.512 | 1.550 | 2.25 |
| 19 | No circ. | 190.2 | 98.8 | 7.876 | 5.487 | 1.666 | 1.500 | 1.35 |
| 20 | Circulated | 198.4 | 102.3 | 8.066 | 6.918 | 1.695 | 0.252 | 2.3 |
| 21 | Circulated | 100.3 | 217.7 | 5.442 | 6.361 | 1.225 | 0.035 | 2.4 |
| 22 | Circulated | 193.0 | 98.0 | 6.623 | 5.101 | 2.194 | 0.038 | 1.75 |
| 23 | Circulated | 187.9 | 92.0 | 5.135 | 4.472 | 1.824 | 0.025 | 1.25 |
| | Large cell | | | | | | | |
| 26 | Circulated | 202.5 | 95.6 | 28.195 | 24.105 | 9.004 | 1.851 | 5.0 |
| 27 | Circulated | 100.2 | 197.0 | 18.187 | 21.267 | 7.412 | 0.00 | 4.7 |
| 28 | Circulated | 292.8 | 98.8 | 29.479 | 23.609 | 8.702 | 0.00 | 5.0 |
| 29 | Circulated | 199.2 | 222.0 | 25.713 | 24.669 | 8.157 | 0.381 | 5.9 |

It has been assumed that the lines at λ 1839.3 and λ 1864 were not absorbed by oxygen. Low initial intensity and poor transmission by quartz would dispose of the first of these, and the second may be evaluated from the geometry of the system and the molecular extinction coefficient of oxygen at λ 1860, which is 0.2.[10] Oxygen at 200 mm. in the 52-mm. vessel was preceded by an air path of 300 mm., and the fraction of light absorbed in the vessel was 0.0056. It therefore appeared unnecessary to assume any primary activation of oxygen.

After illumination the gases were dried by pumping over the potassium hydroxide, and the ammonia was frozen in the trap T by surrounding it with liquid air. The residual oxygen was supplemented by additions from the buret and hydrogen was burned by pumping the mixture over the platinum wire in C, which was heated to a dull redness. Then hydrogen was added in the same manner and oxygen was determined by continuing the combustion. The remaining gas was taken as nitrogen, after deducting the excess unused hydrogen. These gases were pumped off and the ammonia was evaporated and dried. All pressures were corrected to 25° and a correction was made for the added volume of the drying trap. The reaction vessel was removed and rinsed into a volumetric flask, and the drying trap was treated in the same manner. These solutions were found to be largely ammonium nitrate. Hydroxylamine was repeatedly shown to be absent by testing with a solution of copper oxide in strong potassium hydroxide.[11] Nitrous acid was determined by the colorimetric method of Griess.[12] Nitric acid was determined by the phenol–disulfonic acid method,[13] using hydrogen peroxide to oxidize the nitrous acid. The resulting total nitrogen is reported as ammonia nitrate, since the nitrite accounted for less than 1% of the ammonia oxidized. Blanks were run on all reagents used.

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(10) A. Kreusler, *Ann. Physik*, **4**, **6**, 412 (1910).

(11) J. W. Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," Longmans, Green & Co., London, 1928, Vol. VIII, p. 295.

(12) Treadwell and Hall, "Analytical Chemistry," John Wiley & Sons, New York, 1928, seventh edition, Vol. II, p. 306.

(13) Chamot, Pratt and Redfield, THIS JOURNAL, **33**, 381 (1911).

## Experimental Results

**Equation for the Reaction.**—Table I presents the results obtained from analyses, from which we have constructed an equation for the reaction.

To utilize these results, we next calculated the ratios of the products and of oxygen used to the ammonia used, and the quantum yield. These are shown in Table II.

TABLE II

| No. | $O_2$ used | $N_2$ | $H_2$ | $NH_4NO_3$ | Quantum yield |
|---|---|---|---|---|---|
| 18 | 0.750 | 0.216 | 0.225 | 0.32 | 0.57 |
| 19 | .696 | .212 | .190 | .17 | .83 |
| 20 | .857 | .210 | .031 | .29 | .68 |
| 21 | 1.169 | .225 | .064 | .44 | .41 |
| 22 | 0.771 | .331 | .058 | .26 | .81 |
| 23 | .872 | .356 | .048 | .24 | .62 |
| 26 | .855 | .320 | .066 | .19 | .83 |
| 27 | 1.171 | .408 | .00 | .25 | .54 |
| 28 | 0.800 | .295 | .00 | .17 | .92 |
| 29 | .961 | .318 | .015 | .23 | .76 |
| Calculated for equation (1) | | | | | |
| | 0.875 | 0.250 | .. | 0.25 | |

It is obviously impossible to derive for these data an exact equation for the over-all photochemical reaction, and it would be necessary in any case to represent the empirical equation as a series of consecutive reactions. The equation which seems to fit the data best is

$$8NH_3 + 7O_2 \longrightarrow 2N_2 + 2NH_4NO_3 + 8H_2O \qquad (1)$$

but the variations of the values given above from those required by equation (1) need some discussion.

Of the reactions which will probably occur in the system, those whose sum is equation (1) are as follows

$$NH_3 + h\nu \longrightarrow NH_2 + H \qquad (2)$$
$$2H + {}^1/{}_2O_2 \longrightarrow H_2O \qquad (3)$$
$$NH_2 + O_2 \longrightarrow NO + H_2O \qquad (4)$$
$$2NO + O_2 \longrightarrow 2NO_2 \qquad (5)$$
$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3 \qquad (6)$$
$$HNO_3 + NH_3 \longrightarrow NH_4NO_3 \qquad (7)$$
$$HNO_2 + NH_3 \longrightarrow NH_4NO_2 \qquad (8)$$
$$NH_4NO_2 + h\nu_1 \longrightarrow N_2 + H_2O \qquad (9)$$

Many of these reactions are probably complex in themselves, involving such radicals as $NH_2$, NH, NOH, OH and $HO_2$, but the system is too complicated to make a treatment of the intermediates profitable. Evidence for (2), the primary photochemical reaction, has been mentioned. Its reversal exists[14] and may be of importance in explaining the quantum yield:

$$H + NH_2 \longrightarrow NH_3 \qquad (10)$$

Reactions (3), (6), (7) and (8) are familiar and need no discussion. Reaction (4) is energetically probable, and (5) goes practically to completion at the pressures used.

The photolysis of ammonium nitrite according to (9) is reported by Berthelot and Gaudechon[15] to be rapid in solution. The authors have also found that a solid film deposited by sublimation is readily decomposed by monochromatic light in the region of λ 2080. Spectrographs of an 8 mm. thickness of approximately 0.35 molal solution show complete absorption below λ 2500; hence $h\nu_1$ is used.

Hydrogen is formed by a reaction which competes with (3) and reduces oxygen consumption by half the amount of hydrogen found

$$H + H \longrightarrow H_2 \qquad (11)$$

This plays a minor role unless the oxygen becomes exhausted, either in the system as a whole or locally because of lack of circulation. The latter condition obtained in experiments 18 and 19. A low final ammonia pressure, on the other hand, may leave some free nitrous and nitric acids which appear later in the drying trap. Since less ammonia is thereby used, the ratios of all quantities to ammonia will be increased and the quantum yield will be low. This variation is seen in experiment 21.

A decrease in the oxygen used and an increase in the nitrogen produced may be expected from the photolysis of ammonium nitrate, which occurs in solution[15] and may do so in the solid state

$$NH_4NO_3 + h\nu_2 \longrightarrow O_2 + NH_4NO_2$$
$$NH_4NO_2 + h\nu_1 \longrightarrow N_2 + 2H_2O \qquad (12)$$

The film deposited during the reaction has been shown to be mostly ammonium nitrate, and its absence from the illuminated portion has been mentioned. Experiments 22, 23, 26 and 28 show this reaction especially.

Experiments 27 and 29 were begun with a large excess of oxygen, and the oxygen consumption was abnormally high while the nitrate is normal, and it appears that the determination of final oxygen by combustion was incomplete. The residue thus escaping detection would be taken as nitrogen, which is also high in these experiments.

In experiments conducted with the small vessel more nitrate was found in the drying trap than in the vessel, while the reverse was true when the large vessel was used. This suggests that a nitrate solution in the form of a mist—whose ob-

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[14] Melville, *Trans. Faraday Soc.*, **28**, 885 (1932).

[15] Berthelot and Gaudechon, *Compt. rend.*, **152**, 523 (1911).

servation has been described above—was pumped through the system and deposited on the potassium hydroxide as water was removed. In the large cell it settled more completely because of the reduced velocity of flow.

**Light Absorption by Ammonia.**—The absorption coefficients of ammonia have not been determined previously and were necessary for the interpretation of rate curves. Accordingly values of $I/I_0$ were determined for the monochromatic radiation previously described, using the 8-mm. cell and pressures of ammonia from 3 mm. to 340 mm. From a plot of $I/I_0$ against pressure a series of convenient values was taken and for each the absorption coefficient was calculated. The value of $\alpha$ decreased as the pressure was raised, but in spite of this departure from Beer's law it seemed that the data might fit an equation such as $\log I/I_0 = -\alpha p^n t$. To relate the observed coefficients to the new $\alpha$ and to $n$, the equation $\alpha_1 p = \alpha_2 p^n$ was written $\log \alpha_1 p - n \log p = \log \alpha_2$. With a plot of $\alpha_1 p$ and $\log p$ against pressure, trial values of $n$ were used until one was found which made $\log \alpha_2$ linear. The absorption of ammonia is represented to within 1% by the equation when $\alpha = 0.010098$ and $n = 0.76$ if $p$ is in millimeters of mercury and $t$ is in centimeters. The observed and calculated absorption is shown in Fig. 2.

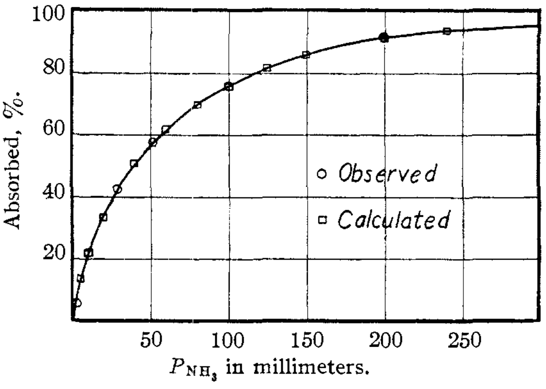

Fig. 2.—Light absorption of ammonia as a function of pressure: thickness, 0.8 cm.; region of λ 2080.

**Rate Curves.**—With the coefficient thus obtained, the curves of Fig. 3 were chosen as being nearly free from the influence of decreasing energy absorption. The first upward bend is "autocatalytic" in form, and indicates a rate proportional to one or more of the products—probably the water needed for reaction (6). A magnifying factor is the increasing solubility of ammonia. The following straight portion, which makes up most of the curve, shows the domination of a zero order reaction; this is thought to be the primary process (2) which is dependent only on the rate of energy supply. The final falling off of the rate is not associated with decreasing light absorption, for it persists when this effect is negligible, as in the large vessel. The rate probably becomes dependent on a reaction requiring a three-body collision, such as (5) or (6).

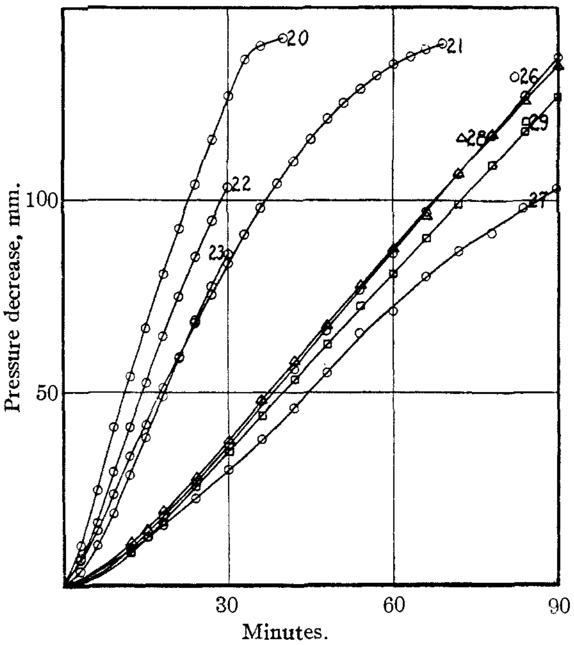

Fig. 3.—Reaction rate curves.

**Quantum Yield.**—The radiation which effects the primary process is also absorbed by ammonium nitrite and nitrate, and reflected and scattered by the film and the mist which have been described. Moreover, the primary process is reversible. Hence the yield of 1.33 molecules of ammonia oxidized per quantum absorbed, which is predicted by the mechanism leading to (1), will be reduced by these factors to an extent which cannot be estimated and which will be variable. The yields shown in Table II are all less than unity, but they have little fundamental significance, although they are in error by not more than 10%.

**Other Experimental Work.**—Both Berthelot and Gion[16] found ozone to be present in studies of this reaction in the light from the mercury arc. Obviously the lines λ 1849 and λ 1942 were absorbed by oxygen as well as ammonia, and the reaction mechanism must have been different

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(16) Gion, *Compt. rend.*, **195**, 421 (1932).

from that proposed here. Berthelot exposed the entire reaction vessel for long periods and it is not surprising that no nitrates or nitrites were found, since both are decomposed photochemically.

## Summary

1. The reaction of ammonia and oxygen in radiation from the zinc spark has been studied, and a chemical equation for the reaction has been derived from analyses of the products.

2. A reaction mechanism leading to the empirical equation is proposed and probable side reactions are considered; these are discussed in their relation to analytical results and to the form of the rate curve.

3. An empirical modification of Beer's law has been derived, which represents absorption by ammonia in the region of $\lambda$ 2080.

4. The quantum yield in the reaction has been found variable, and reasons for the variation have been advanced.

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[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, AT THE UNIVERSITY OF CALIFORNIA]

# The Heat Capacities at Low Temperatures of the Alkaline Earth Carbonates[1]

BY C. TRAVIS ANDERSON[2]

In a previous paper from the Pacific Experiment Station of the United States Bureau of Mines the author presented low-temperature thermal data for some carbonates in the first periodic group. The present paper deals with the carbonates of calcium (calcite and aragonite), strontium and barium.

The method, apparatus and accuracy have been described previously.[3]

## Materials

In Table I are shown the materials used. The −14 +35 mesh size of all the materials was prepared by simple crushing and separation by standard screens of selected, well-developed crystals. The finer sample of calcite was prepared by grinding in a mechanical agate mortar with frequent classification by means of an air elutriator, arranged as described by Roller.[4] The particle size of the final product was determined by microscopic means to average near 0.5 micron. It had a very low apparent density and was compressed into pellets at a pressure of about 2 tons per sq. in., so that an adequate amount of the material could be put into the calorimeter, and also to improve the thermal conductivity. The fairly dense pellets which were produced were again crushed to −14 +35 mesh size.

The calcite and aragonite were analyzed by thermal decomposition at 1000° in a slow stream of pure dry nitrogen, determining the carbon dioxide and water evolved, and loss in weight of the sample. Analysis of the coarse sample of calcite showed a carbon dioxide content of 43.959%, with an approximate correction to vacuum, against the theoretical content of 43.972%. Calculation from the carbon dioxide content of the fine material showed only 98.656% $CaCO_3$. No silica could be detected. Since the weight of carbon dioxide and water checked the loss in weight of the calcite during decomposition, the composition of the impurity was calculated to consist only of $Ca(OH)_2$ and $H_2O$, the actual figures being 0.726% $Ca(OH)_2$ and 0.618% $H_2O$. In correcting the specific heats the water was calculated as ice.[5]

Precise density determinations were made on the samples using carbon tetrachloride of high purity. The correction for the density of the fine materials was obtained by making a rough density determination on a sample of lime, hydrated with an amount of water corresponding to the analysis of the impurity.

## The Specific Heats

The experimental results obtained for the two samples of calcite are presented in Table II, aragonite in Table III and strontianite and witherite in Tables IV and V, respectively. The data given as gram-calories (15° per gram formula

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(1) Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

(2) Assistant Physical Chemist, U. S. Bureau of Mines, Pacific Experiment Station, Berkeley, California.

(3) Anderson, THIS JOURNAL, **52**, 2296, 2712 (1930); **54**, 107 (1932); **55**, 3621 (1933).

(4) Roller, U. S. Bureau of Mines Tech. Paper 490 (1931).

(5) Anderson, THIS JOURNAL, **52**, 2712 (1930).