Summary

1. The densities and surface tensions of nicotine have been measured from −50 to 94° and of nicotine–water solutions from −50 to 60°.

2. The Eötvös constant for nicotine is shown to be between 2.4 and 2.8 and nicotine does not appear to be associated.

3. Evidence for the existence of nicotine hydrates is shown by the concentration–surface tension curves.

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[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE DISSOCIATION PRESSURE OF Fe_4N

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Introduction

In order to learn more concerning the various factors that contribute to the remarkable efficiency of promoted iron catalysts for the production of synthetic ammonia, a number of workers have investigated the conditions under which nitrides of iron can be formed. Baur and Voerman,[1] Maxted[2] and others tried without success to form iron nitride by the action of nitrogen at pressures as high as 200 atmospheres on iron between temperatures of 400 and 700°. Noyes and Smith[3] showed the possibility of calculating the exact dissociation pressure of the iron nitrides by combining the equilibrium constants for the reactions

$$N_2 + 3H_2 = 2NH_3 \qquad K_1 = \frac{(P_{NH_3})^2}{(P_{H_2})^3(P_{N_2})} \qquad (1)$$

$$2Fe_xN + 3H_2 = 2xFe + 2NH_3 \qquad K_2 = \frac{(P_{NH_3})^2}{(P_{H_2})^3} \qquad (2)$$

to obtain K_3 for the reaction

$$2Fe_xN = 2xFe + N_2 \qquad K_3 = P_{N_2} = \frac{K_2}{K_1} \qquad (3)$$

At 460° the indirect values thus obtained were found to vary between 20,000 and 500,000 atmospheres, depending upon the nature of the solid phase.

The surface hardening of complex alloy steels by treatment with ammonia at elevated temperatures enhances interest in equilibria for the iron–nitrogen system. Recent x-ray structure investigations by Hägg,[4] by Brill[5] and by Osawa and Iwaizumi[6] of the compounds formed by the action

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[1] Baur and Voerman, *Z. physik. Chem.*, **52**, 467 (1905).

[2] Maxted, *J. Soc. Chem. Ind.*, **37**, 105 (1918).

[3] Noyes and Smith, THIS JOURNAL, **43**, 475 (1921).

[4] Hägg, *Nature*, 121, 826 (1928).

[5] Brill, *Z. Kryst.*, **68**, 378 (1928).

[6] Osawa and Iwaizumi, *ibid.*, **69**, 26 (1928).

of dry ammonia on iron indicated that Noyes and Smith were probably dealing with mixtures of more than two solid phases and that the compounds actually present in their experiment were Fe_4N, Fe_2N and perhaps Fe_3N, but not in addition, the postulated Fe_8N and Fe_6N. Frankenburger[7] reports that some specimens of iron catalyst when removed from high pressure ammonia converters contain as much as 5% of nitrogen. Accordingly, since the value of the ratio $(P_{NH_3})^2/(P_{H_2})^3$ known to exist in the high pressure ammonia conversions is very much lower than the value found by Noyes and Smith for K_2 at 460°, it is probable either that K_2 changes very rapidly with temperature or else is very much lower than reported. It seemed to be worth while to determine the values of K_2 at several different temperatures, taking care to identify the solid phases by means of their x-ray powder diffraction patterns.

The present paper recounts the determination of the value of the equilibrium constant for the reaction

$$2Fe_4N + 3H_2 = 2NH_3 + 8Fe \quad K_4 = \frac{(P_{NH_3})^2}{(P_{H2})^3} \tag{4}$$

at 420, 444, 460 and 525°. The dynamic method used consisted in passing various mixtures of ammonia and hydrogen over iron at a fixed temperature and noting the gas composition at which the first nitride formation occurred. The solid phases present at equilibrium were identified by x-ray powder diffraction patterns. From the data obtained the value for the equilibrium constant of the reaction

$$2Fe_4N = N_2 + 8Fe \quad K_5 = P_{N_2} \tag{5}$$

has also been determined.

Apparatus and Experimental Procedure

A flow system apparatus was designed that permitted the passage of a hydrogen-ammonia mixture of definite composition over a sample of iron at a fixed temperature. Tank hydrogen was purified by passage over hot copper and through a phosphorus pentoxide tube. The purified gas analyzed 99.9% of hydrogen in a Bone and Wheeler gas analysis apparatus. The synthetic ammonia used was dried by contact with metallic sodium; it did not contain appreciable free nitrogen or hydrogen. Calibrated flowmeters permitted mixing the two gases in any desired proportion immediately before passing them over the iron sample. The iron used was obtained by the reduction of c. p. ferric oxalate in hydrogen.

The glass reaction vessel as shown in Fig. 1 consisted of reaction chamber A with its inlet and outlet, side tube B, for inserting the charge of ferric oxalate, thermocouple well C, extending through the entire sample and side tube D for taking samples for the x-ray photographs. It was heated by a nichrome wire-wound heating furnace controlled by hand-adjusted rheostats. The variation in temperature never exceeded ±5° during a run. In the experiments carried out at 444° the furnace was replaced by a sulfur bath; the temperature in these runs was constant to within ±0.5°. All tem-

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[7] Frankenburger, Ullmann "Enzyklopädie der Technischen Chemie," p. 393 (footnote), Berlin, 1928.

peratures were determined with a calibrated alumel–chromel thermocouple in conjunction with a Leeds and Northrup portable potentiometer.

The procedure used in each experiment is briefly described below. A weighed charge of ferric oxalate was introduced into the reaction tube and reduced in a stream of hydrogen. After complete reduction of the sample, as determined by absence of water vapor in the exit gases and by x-ray powder photographs, various mixtures of ammonia and hydrogen were passed over it for definite periods of time at a fixed temperature. The composition of the gaseous mixture used was checked at the beginning of each run, both before and after it passed over the iron, by absorbing the ammonia in 4% boric acid and measuring the hydrogen in a gas compensometer. The ammonia absorbed in the boric acid was titrated with standard sulfuric acid using methyl orange as indicator. At a flow of approximately 400 cc. of gas per minute, used in all runs, no cracking was observed on the 1- or 2-g. samples of iron.

Upon completion of an experiment, pure nitrogen was run over the sample for a few seconds to flush out the hydrogen–ammonia mixture; the tube was then quickly cooled in a stream of nitrogen by removing it from the furnace. Finally, an x-ray sample was shaken into the thin-walled side tube D and sealed off. The remaining sample in the reaction vessel was reduced in a current of hydrogen, the temperature being gradually raised from 25 to 525°. The ammonia formed was usually determined as described above; in those runs, however, in which only a small amount of nitride was anticipated, water was used as an absorbent and titrations were carried out with 0.01 *N* sulfuric acid using sodium alizarine sulfonate as indicator.

The x-ray powder diffraction photographs were all taken with iron K radiation obtained from a metal tube operated at 5 to 20 milliamperes and 20,000 to 30,000 volts. An oxide coated filament was used in order to prevent contamination of the anticathode; nevertheless, the anticathode was frequently cleaned. A small cylindrical camera of 3.583-cm. radius was used throughout the work. Sodium chloride and iron were used as reference substances for accurate spacing determinations. With this apparatus a few per cent. of Fe_4N could be detected in an iron sample.

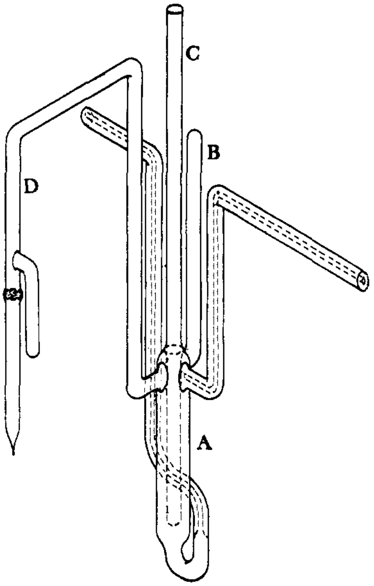

Fig. 1.

Results

The results of the equilibrium studies are listed in Table I. The fourth column of this table indicates that some nitrogen was present in the sample even when the percentage of ammonia used in the gaseous mixture was not high enough to produce Fe_4N. The nature of this small amount of nitrogen is not well understood. It is possible that part of it is due to ammonia sorbed by the iron and not removed by the thirty-second flushing with nitrogen. Probably, however, most of it is to be accounted for by the formation of a surface nitride, analogous to a previously discussed[8] surface oxide formation occurring when mixtures of steam-hydrogen containing less than the equilibrium percentage of steam are passed over freshly reduced iron, cobalt or nickel. The assumption that this blank is due to a solid solution of nitrogen with iron is improbable, as will be pointed out later.

TABLE I

SUMMARY OF EQUILIBRIUM RUNS

Rate of flow, 400 cc. per min.

Temp., °C.	Time of run, hours	NH_3 in gas mixture, %	N_2 collected, mg.	X-ray diffraction pattern
			Sample I.	Weight of iron, 1.19 g.
460	5	25	2.4	Pure Fe, complete absence of Fe_4N
	3	27	2.7	Fe_4N entirely absent
	1	28	1.6	No photograph
	1	29	9.6	No photograph
	3.5	29	52.0	Very strong Fe_4N lines, faint Fe lines
	10	29	55.3	Very strong Fe_4N lines, very faint Fe lines
525	5.5	15	3.5	No photograph
	4	16	4.3	Fe_4N completely absent
	4	17	4.8	Fe_4N completely absent
	3.5	17	7.1	Very faint Fe_4N lines
	2	17.5	10.6	Fe_4N lines present with strong Fe lines
	4	17.5	13.5	Fe_4N lines indicating about 25% Fe_4N
	4	19	25.7	About 50–60% Fe_4N
			Sample II.	Weight of iron, 1.78 g.
420	4	35	5.8	Extremely faint Fe_4N
	4	36	2.8	Fe_4N completely absent
	4	37	7.0	Distinct Fe_4N lines
	5	38	23.7	About 20% Fe_4N
	5	39	21.1	About 20% Fe_4N
	5	40	13.8	Distinct Fe_4N lines
444	4	29	2.1	Fe_4N completely absent
	4	30	5.7	Distinct Fe_4N lines present
	3	31	8.7	Distinct Fe_4N lines present
460	4	28	2.8	No photograph

Table II shows the equilibrium data deduced from the results listed in Table I. The ammonia percentage in a hydrogen-ammonia mixture

TABLE II

EQUILIBRIUM DATA OF THE REACTION $2Fe_4N + 3H_2 = 8Fe + 2NH_3$

Temp., °C.	% NH_3 in equilibrium	$K = \frac{(NH_3)^2}{(H_2)^3}$
420	36 ± 1.5	0.495 ± 0.08
444	30 ± 1	.262 ± .03
460	28.5 ± 1	.223 ± .025
525	17 ± 1	.051 ± .01

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[8] Emmett and Shultz, THIS JOURNAL, **51**, 3249 (1929).

in equilibrium with Fe–Fe_4N at each temperature is given in Col. 2. The calculated equilibrium constants are listed in Col. 3.

The results of the x-ray examinations are listed in the fifth column of Table I. The only phases present, as indicated by the diffraction photographs, are Fe and Fe_4N. Measurements, using sodium chloride as a reference substance, of the diffraction lines from the iron and the Fe_4N lattices are in agreement with the results obtained by previous investigators, with the exception of Osawa and Iwaizumi. A typical set of x-ray diffraction data from Fe_4N is given in Table III. The average value of a_0 from our measurements for Fe_4N is 3.79_4 Å. The average value obtained by passing 38% NH_3 over iron at 420° is 3.79_0 Å.; 29% NH_3 at 460° is 3.79_6 Å.; 39% NH_3 at 420° is 3.79_0 Å. The variations noted are within the experimental error.

TABLE III

TYPICAL X-RAY DIFFRACTION DATA FROM Fe_4N. Fe K RADIATION

Intensity	$\theta/2$	d_{hkl}, Å.	Indices	a_0, Å.
Medium	23° 34′	2.192	111 β	3.797
Very strong	26° 31′	2.189	111	3.791
Medium weak	27° 31′	1.897	200 β	3.794
Medium strong	30° 40′	1.896	200	3.792
Medium weak	40° 53′	1.340	220 β	3.790
Strong	46° 7′	1.341	220	3.793
Medium	50° 2′	1.143	311 β	3.791
Very strong	57° 47′	1.143	311	3.791
Medium	62° 3′	1.095	222	3.793

The diffraction data of Fe_4N can be explained by a cubic lattice containing 1 Fe_4N with the iron atoms at $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, 000 and the nitrogen atom at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The nitrogen atoms alone contribute to reflections from planes (*hkl*) with one or more indices even in odd orders; such reflections should be relatively very weak. An overexposed x-ray photograph of a sample obtained by passing a 29% NH_3 gas mixture over iron at 460° and shown by analysis to contain about 90% Fe_4N, indicated the presence of the reflection from (100). The experimental procedure was not sufficiently refined, however, to allow observation of two other reflections, namely, those from (110) and (210), reported by Brill.[9]

Samples of the solid phases from one-hour runs at 460° with 31, 30, and 20% of NH_3, respectively, were mixed with an equal amount of pure iron obtained by reduction of the oxalate. These powder mixtures gave patterns showing no broadening of the diffraction lines. It is estimated that a change in the lattice constant of one part in one thousand could easily be observed by this method. This is in disagreement with the results of Osawa and Iwaizumi,[6] who reported as great as 1% distortion of the edge of the unit cube for alpha iron in a system containing small amounts

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[9] Brill, *Z. Krist.*, **68**, 379 (1928).

of nitrogen. They suggested that the nitrogen was in solid solution in the iron. Under the conditions of our experiments there is surely no x-ray evidence for the existence of such a solid solution.

It is difficult to calculate accurately the maximum possible error that might exist in any one reading. However, allowing liberally for possible errors in the rates of flow of hydrogen, and of ammonia, and in the temperature of the material in the reaction vessel, we estimate that the greatest deviation at each temperature that could arise even if all of the errors by chance happen to be in the same direction is such as to give for the final percentage ammonia in the equilibrium ammonia–hydrogen mixture the values 36.5 ± 3.3 at 420°, 30 ± 1.5 at 444°, 28.5 ± 2.7 at 460° and 17.0 ± 1.8 at 525°. However, consideration of the number of runs made at each temperature and of the agreement obtained leads us to believe that the equilibrium values at each of the four temperatures can be confined to narrower limits. These limits are, as listed in Table II, 36 ± 1.5 at 420°, 30 ± 1 at 444°, 28.5 ± 1 at 460° and 17 ± 1 at 525°. In Fig. 2 is shown a plot of log K_4 values against $1/T$.

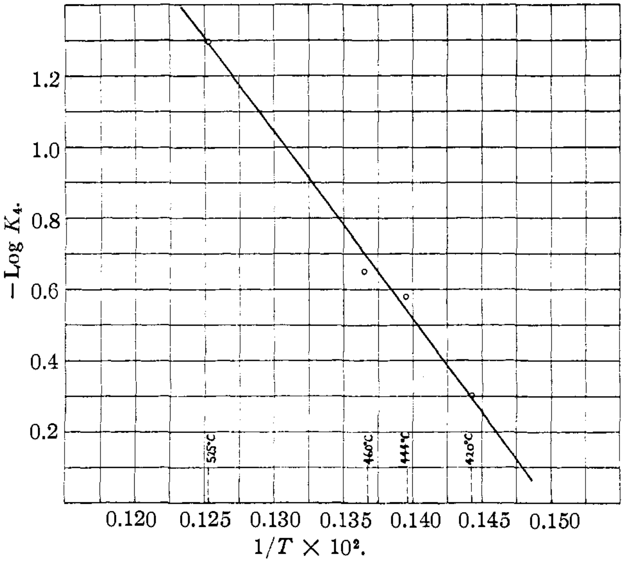

Fig. 2.—Variation of $-\log K_4$ with $1/T$.

Thermodynamic Calculations.—The dissociation pressure of Fe_4N can be calculated, as already described, by combining the known equilibrium constant for Reaction 1 with the present determined constant for Reaction 4. Thus for Reaction 5 the value of $K_5 = P_{N_2} = K_4/K_1$ will vary from 4250 atm. at 420° to 5600 atm. at 525°, as can be seen by reference to Table IV. The values of K_1 are those obtained by the use of the equation given by Haber[10] for one atmosphere equilibrium values for Reaction 1.

$$\log K_1 = \frac{26{,}400}{4.571\ T} - 12.268$$

Due to the lack of any data for the specific heat of Fe_4N, it does not seem desirable to include in the present discussion even approximate values for ΔH_{298}, or ΔF_{298} for Reactions 4 and 5. It may be pointed out, however, that the average value for ΔH for Reaction 4 between 420 and 525° obtained from the slope of the curve in Fig. 2, corresponds to $-24{,}100$ calories.

TABLE IV

THE DISSOCIATION PRESSURE OF Fe_4N

Temp., °C.	$K_1 = \frac{(P_{NH_3})^2}{(P_{H_2})^3(P_{N_2})}$	$K_4 = \frac{(P_{NH_3})^2}{(P_{H_2})^3}$	$K_5 = \frac{K_4}{K_1} = P_{N_2}$
420	11.61×10^{-5}	0.495	4250
444	6.12×10^{-5}	.262	4300
460	4.12×10^{-5}	.223	5400
525	0.92×10^{-5}	.051	5600

Discussion

The calculated dissociation pressures obtained in the present paper are entirely consistent with the failure of all direct attempts to synthesize Fe_4N from nitrogen and iron by exposure of the latter to nitrogen at as high pressures as 200 atmospheres, at temperatures between 400 and 700°.

The equilibrium values obtained by us are markedly lower than the value obtained by Noyes and Smith for the systems of low nitrogen content. Thus we found K_4 to be 0.223 at 460°, corresponding to a dissociation pressure of 5400 atmospheres for Fe_4N. Noyes and Smith found K_2 to be unity at 460°, the corresponding dissociation pressure for Fe_xN being 20,000 atmospheres. It seems highly probable that their various Fe_xN samples in which the iron–nitrogen atomic ratios were between 17:1 and 8:1 were mostly Fe_4N and Fe with small amounts of Fe_3N or Fe_2N.

In each of the twenty to thirty minute experiments made in the static system employed by Noyes and Smith, the small amounts of higher nitrides, either because of their probable location on the outer boundary of the Fe_4N–Fe particles, or because of their greater rate of reduction by hydrogen, could rapidly remove a large portion of the hydrogen in the gas mixture and could thereby cause the final value of the ammonia–hydrogen ratio to be too high. Thus the equilibrium values given by Noyes and Smith may be too high, due to the partial or complete establishment of equilibrium between H_2–NH_3–Fe–(Fe_2N or Fe_3N) or H_2–NH_3–Fe_4N–(Fe_2N or Fe_3N) rather than between H_2–NH_3–Fe–Fe_4N as in the present

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[10] Haber, *Z. Elektrochem.*, 21, 89 (1915).

work. In any case, the present experimental values can be relied upon to represent within the limits of error already outlined the equilibria of Reactions 4 and 5.

It may be well to point out a few conclusions from the above work that will be of interest to those concerned with the nitrogen content of steels. The minimum amount of ammonia in a mixture of ammonia and hydrogen that when passed over steel will form a layer of Fe_4N varies from 17% at 525° to 36% at 420°. Intermediate temperatures can be obtained indirectly from the curve of Fig. 2. Contrary to the opinions of many metallurgists,[11] there is no evidence that the liberation of "nascent nitrogen" by ammonia cracking permits ammonia to be more effective as a nitriding agent than pure nitrogen; rather, it may be said that thermodynamically the reverse of Reaction 2 above will occur whenever the ammonia–hydrogen ratio in the mixture above the iron sample exceeds the equilibrium ratio.

The iron–nitrogen "phase rule diagram" as given by various metallurgists[11] and also pictured in the "International Critical Tables"[12] is not in any sense an "equilibrium diagram" if nitrogen at one atmosphere pressure is considered as the gas phase. Such thermal studies as have been made are possible only because of the low rate of decomposition of the nitrides formed.

The increase of the dissociation pressure of Fe_4N with temperature over the temperature range 420 to 525° indicates that alpha iron will not react at any temperature with nitrogen to form Fe_4N. It is at present not clear how the nitride needles reported[13] to be formed by melting iron in nitrogen and quenching suddenly can actually result from the combination of iron and nitrogen. It is possible, however, that gamma iron existing between 920 and 1430° may either possess a different reactivity toward nitrogen or enter into a series of solid solutions with Fe_4N. It is also possible that although the dissociation pressure of Fe_4N and the nature of its change with temperature may preclude the possibility of its being formed by the reaction of nitrogen at one atmosphere pressure with alpha iron, nevertheless, the dissociation pressure of Fe_3N or Fe_2N may change with temperature in such a manner as to make the formation of one of these latter nitrides possible. These systems are now being investigated.

Summary

The equilibrium constants for the reaction $2Fe_4N + 3H_2 = 8Fe + 2NH_3$ have been determined to be 0.495 ± 0.08, 0.262 ± 0.03, 0.223

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[11] Nitriding Symposium, A. S. S. T., XVI, October, 1929.

[12] "International Critical Tables," Vol. II, p. 451.

[13] R. S. Dean, R. O. Day and J. L. Gregg, Technical Publication No. 193, Am. Inst. of Mining and Metallurgical Engineers; C. Baldwin Sawyer, Transactions of A. S. S. T., September, 1925, p. 291.

± 0.025 and 0.051 ± 0.01, at 420, 444, 460 and 525°, respectively. From these constants, together with the equilibrium constants for the N_2–H_2–NH_3 system, the dissociation pressures of Fe_4N according to the reaction $2Fe_4N = 8Fe + N_2$ have been calculated to be 4250, 4300, 5400 and 5600 atmospheres, respectively, at the above temperatures. The solid phases were identified as Fe_4N and Fe by means of x-ray powder photographs. They give no indication of any distortion of the iron lattice as might possibly result if under the condition of our experiments appreciable solution of nitrogen in the iron samples were to occur. The results explain many but not all of the phenomena observed in the nitriding of steels.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 2]

A STUDY OF THE REACTION OF HYDROGEN BROMIDE WITH SILICON

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Although the facts concerning the reaction of hydrogen bromide upon silicon at elevated temperatures have long been known in a general way, and the similarity of this reaction to that of hydrogen chloride upon silicon has been pointed out, especially by the work of such investigators as Buff and Wöhler,[1] Gattermann,[2] Besson and Fournier,[3] and Combes,[4] no very precise data concerning the necessary conditions, the purity of the materials used, the yields of the various products and the mechanism of this reaction appear to have been laid down; the present investigation was undertaken with the object of throwing further light upon these and allied matters. Inasmuch as a mixture of products is inevitably obtained, and the separation by fractionation of the crude product by the usual methods of distillation is not particularly clean-cut, the boiling points of the bromine derivatives of silane given by the different earlier observers mentioned do not agree closely, so that more recently Stock and his coworkers,[5] starting with silane, have prepared these compounds and determined their constants with greater accuracy.

The apparatus used in the present study of the reaction of gaseous hydrogen bromide with crystalline silicon is shown in Fig. 1.

Electrolytic hydrogen was passed through three towers (two of which appear in the figure) containing fused flakes of potassium hydroxide, thence it could be passed directly

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[1] Buff and Wöhler, *Ann.*, **104,** 99 (1857).

[2] Gattermann, *Ber.*, **22,** 193 (1889).

[3] Besson, *Compt. rend.*, **112,** 530 (1891); Besson and Fournier, *ibid.*, **151,** 1055 (1910).

[4] Combes, *ibid.*, **122,** 531 (1896).

[5] Stock and Somiesky, *Ber.*, **50,** 1739 (1917).