

THE JOURNAL
OF THE
American Chemical Society

BEHAVIOR OF THE HYDRONITROGENS AND THEIR DERIVATIVES IN LIQUID AMMONIA. IV. PRESSURE-CONCENTRATION ISOTHERMS IN THE SYSTEM AMMONIA, AMMONIUM TRINITRIDE.¹

By A. W. BROWNE AND A. E. HOULEHAN.

Received April 7, 1913.

The five hydronitrogens that have been isolated up to the present time obviously may be classified as (1) basic, (2) acidic, and (3) saline. Under the first heading are grouped ammonia and hydrazine, under the second hydronitric acid, and under the third ammonium trinitride and hydrazine trinitride. In view of the marked tendency shown by many salts to form ammonates and hydrazinates it seems reasonable to suppose that the saline hydronitrogens also might under proper conditions form addition products with ammonia, hydrazine, and hydronitric acid. Such ammonates, hydrazinates, and azoimidates would be of particular interest from the fact that they would themselves be hydronitrogens, or binary compounds containing only nitrogen and hydrogen.

The present article contains the record of a series of experiments made upon the two-component system ammonia, ammonium trinitride. Pressure-concentration isotherms have been studied at 20°, 0°, and -33°. The results are presented under the following headings: (1) apparatus and general method of procedure; (2) details of experiments; (3) discussion of results; (4) summary.

Apparatus and General Method of Procedure.—The apparatus employed in the experiments is shown in Fig. 1. It consists essentially of the cell A connected at the left with the glass-stoppered, water-jacketed Hempel

¹ For the earlier articles of this series see Browne and Welsh, *THIS JOURNAL*, 33, 1728 (1911), and Browne and Houlehan, *Ibid.*, 33, 1734, 1742 (1911).

gas buret *DE*, which is filled with mercury, and at the right with the mercury manometer *H*. The cell is enclosed within the vacuum vessel *B*, which is mounted in a wooden base, and which is closed with a tightly fitting cork stopper. Through openings in this stopper pass the two capillary tubes leading from the cell, an inlet tube for anhydrous liquid ammonia from the steel container *S*, and an outlet tube for waste ammonia

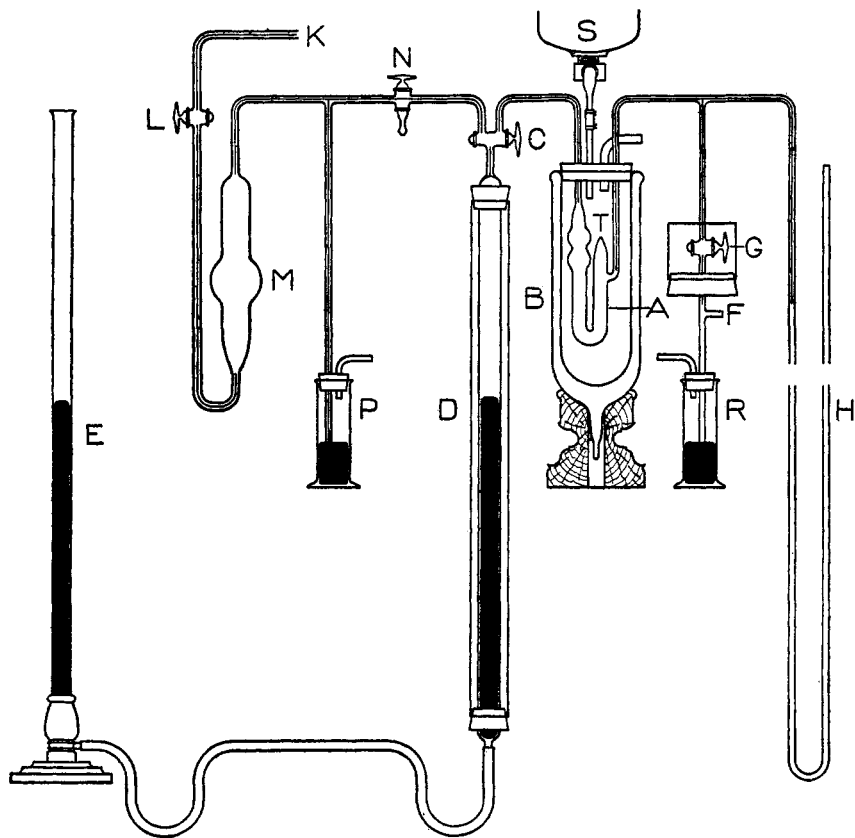


Fig. 1.

gas. The measuring tube *D* of the buret may be brought into connection, by means of the two-way stopcock *C*, either with *A* or, through the three-way stopcock *N*, with the tube *M*. Ammonia is admitted to the apparatus through either *K* or *F*. The mercury traps *P* and *R* serve as safety outlets.

The general procedure adopted in the experiments was briefly as follows. The entire apparatus, which was of course suitably mounted in a rigid wooden frame, was first thoroughly cleaned and dried. The air in the

apparatus was then displaced by means of pure, dry ammonia.¹ After the manometer tube *H* had been filled to the proper level with clean, dry mercury, and the stopcock *G* had been closed, the gas was pumped out of *A*, with the aid of the buret, which was used as a vacuum pump, until a Torricellian vacuum had been reached. The gas drawn into *D* by each stroke was blown out through *P*. Carefully measured small volumes of ammonia were now successively admitted into *A*, which was held at constant temperature by means of a suitable substance in *B*, and the corresponding pressures were read from *H*. By this means the volume of the cell at various pressures—that is, the volume enclosed between the stopcock *C* and the inner mercury meniscus of the manometer—was determined. This procedure was necessary from the fact that in making calculations of the composition of the liquid and solid phases, a correction for the ammonia in the vapor phase must of course be introduced.

The cell was now brought to atmospheric pressure, and was opened by carefully breaking off the tip *T*. A weighed amount of pure ammonium trinitride, prepared by the method already described in an earlier article,² was introduced into the cell, which was then sealed again at *T*, in such a way as to avoid significant change in its volume. After it had again been thoroughly evacuated, the cell was brought to the temperature at which the experiment was to be conducted. For the work at 20°, 0°, and -33°, *A* was respectively immersed in water, packed in ice, and immersed in boiling liquid ammonia. Carefully measured volumes of ammonia gas were successively introduced in each case into *A*, the system being allowed after each addition to reach equilibrium as nearly as possible before the next volume was added.

When the system comprised solid and vapor phases only, equilibrium was in general reached more slowly than when a liquid phase was present, since in the latter case efficient stirring could be effected by alternately introducing and withdrawing a small amount of gas so as to cause it to bubble through the liquid. Special precautions were taken to guard against the presence of air in the ammonia, as this would obviously lead to cumulative error. It was at first considered advisable to condense a considerable amount of ammonia in the tube *M*, with the aid of solid carbon dioxide and ether, and to obtain from this liquid the gas to be introduced into the cell. This precaution was subsequently found to be unnecessary, however, as the ammonia could be obtained from the cylinder free from appreciable quantities of air or other foreign gases. To prevent leakage through the stopcocks at the relatively high pressures that prevailed at times in the

¹ The ammonia used throughout the present research was obtained from Herf and Frerichs, of St. Louis, Missouri, and was found to be of unusual purity. No appreciable amounts of organic bases such as pyridine were found to be present in it.

² THIS JOURNAL, 33, 1742-52 (1911), page 1743.

apparatus, a lubricant composed of certain proportions of paraffin, vaseline, and rubber was used. With the aid of this familiar lubricant, it has been found possible to maintain indefinitely a pressure of four atmospheres in the cell, and a Torricellian vacuum in the buret at the same time, without perceptible leakage. The pressures were developed by simply raising the level tube *E*, which was connected with *D* by means of a sufficiently long and strong piece of black enamelled rubber tubing. As additional precautions against possible leakage the stopcocks were securely wired in position, and a short column of mercury was often introduced into the capillaries above the stopcocks *C* and *G*.

During the introduction of the measured amounts of ammonia, the approximate volume of the liquid and solid phases was noted from time to time, since this volume would of course influence to a slight extent the correction for the amount of ammonia in the vapor phase. In order to facilitate this observation the cell had been roughly calibrated at the outset. After equilibrium had been attained in each case, the corresponding pressure was read from the manometer with the aid of an accurately ruled pasteboard scale which was mounted in permanent fashion against the manometer. Inasmuch as the chief object of the research has been the identification of possible new compounds with the aid of the method of indirect analysis afforded by the pressure-concentration relations in the system, rather than the accurate measurement of absolute pressures, no effort was made to design a more accurate manometer than that just described. With this apparatus the pressures were readily measured with an accuracy of about one millimeter. Corrections for the temperature of the mercury, both in manometer and barometer, were of course introduced when significant. From time to time, during the progress of the system toward a state of equilibrium, the pressure was noted, since from the time-pressure curves taken under these conditions interesting information concerning the state of the system and concerning the transitory formation of metastable or of unstable substances can sometimes be obtained.

After the desired amount of ammonia had been introduced, the procedure was reversed by withdrawing measured volumes of ammonia from the system and reading the pressures after equilibrium had been attained. When the system contained solid and vapor phases only, and the solid was made up of the two phases an ammonous salt and ammonated salt, equilibrium was in general reached more rapidly after gas had been withdrawn than after it had been introduced. This is in all probability attributable to the absence of any marked tendency, during the withdrawing of gas, toward the formation of protective layers that would retard the attainment of equilibrium. During the introduction of gas the formation of protective layers of ammonated salt upon the particles of an ammonous

salt may no doubt readily take place. It is thus apparent that the results obtained by withdrawing gas should be rather more reliable than those obtained by introducing gas. Moreover, if the ammonia should for any reason chance to be contaminated with small amounts of air, or other foreign gases, which would of course raise the pressure higher and higher beyond its normal value during the introduction of the gas, these would be entirely removed during the withdrawal of the first few portions of ammonia from the system.

Details of the Experiments. (a) *The Isotherm at 20°.*—In order to ascertain whether or not ammonium trinitride would show any tendency to form addition products with ammonia at room temperature, the course of the 20° isotherm was first determined up to a pressure of 206 cm. A sample of ammonium trinitride weighing 0.5334 gram was sealed into the cell, which was then completely evacuated. Successive measured portions of ammonia were introduced, with the result that the pressure rose very rapidly, indicating that no absorption of ammonia by the solid phase was taking place. In fact the 20° isotherm of the pressure-concentration diagram was found to rise vertically from the origin, coinciding with the axis of ordinates.

(b) *The Isotherm at 0°.*—After the completion of two preliminary series of measurements, the series recorded in Table I was conducted. The chief difficulty in the work was found to lie in the comparative slowness with which equilibrium was restored, after it had been disturbed by the introduction or withdrawal of ammonia. The observations were made over a period of about four days, during which time the cell was kept packed in ice. The percentages of ammonia recorded in the second column of the table indicate the concentration of that substance in the solid and liquid phases, exclusive of the ammonia in the ammonium trinitride itself, and of that in the vapor phase. A sample of ammonium trinitride weighing 0.5334 gram was used.

TABLE I.

Number of observation.	Concentration of ammonia. Per cent.	Pressure cm. mercury.	Number of observation.	Concentration of ammonia. Per cent.	Pressure cm. mercury.
1	0.06	127.3	14	45.9	149.5
2	4.60	148.3	15	42.1	149.4
3	6.95	149.1	16	37.6	149.4
4	9.9	149.5	17	32.5	149.4
5	15.1	150.3	18	21.7	148.8
6	23.4	150.5	19	19.0	148.7
7	30.3	150.6	20	15.5	148.6
8	36.1	150.7	21	11.9	148.6
9	40.9	150.8	22	8.0	148.4
10	45.2	150.8	23	4.73	148.4
11	54.2	177.3	24	1.86	147.6
12	51.7	158.9	25	1.24	147.3
13	49.4	149.6			

(c) *The Isotherm at -33° .*—Four series of measurements were made, of which but one need be recorded here, since the others give substantially identical results. In Table II are appended the concentrations and pressures observed during the withdrawal of ammonia in successive portions from a system containing at the outset 0.5491 gram of ammonium trinitride and 1.0975 grams of ammonia, exclusive of that in the salt and in the vapor phase.

TABLE II.

Number of observation.	Concentration of ammonia. Per cent.	Pressure cm. mercury.	Number of observation.	Concentration of ammonia. Per cent.	Pressure cm. mercury.
1	66.7	59.1	22	42.0	43.6
2	65.9	56.7	23	39.8	43.1
3	65.1	55.6	24	36.9	39.2
4	64.3	54.4	25	35.8	23.2
5	63.3	52.2	26	36.4	32.8
6	62.1	49.7	27	35.9	22.8
7	61.5	48.6	28	35.3	22.8
8	60.7	47.0	29	34.6	22.8
9	59.9	44.9	30	32.7	22.8
10	59.0	42.8	31	31.1	22.8
11	58.0	40.7	32	29.5	22.8
12	56.9	38.5	33	27.7	22.8
13	55.9	36.2	34	26.0	22.8
14	54.9	34.0	35	24.2	22.8
15	53.8	31.9	36	22.3	22.8
16	52.7	29.8	37	20.6	22.8
17	51.3	43.8	38	18.9	22.8
18	49.7	43.6	39	16.2	22.8
19	48.0	43.6	40	7.86	22.8
20	46.1	43.7	41	5.43	22.8
21	44.1	43.7	42	1.55	22.0

Discussion of Results.—The data presented in Tables I and II have been plotted in Fig. 2. The ordinates are the pressures of ammonia in the system, expressed in centimeters of mercury, and the abscissas are the percentage concentrations of ammonia in the solid phase, apart from the ammonia of the ammonium trinitride itself.

The curve *OABC*, which is the zero isotherm, is composed of three parts. Along *OA*, which coincides with the axis of ordinates, the system is bi-variant, containing solid ammonium trinitride and vapor. Ammonia is not absorbed by ammonium trinitride at 0° until a pressure of about 149 cm. is reached. This is the pressure of the saturated solution of ammonium trinitride in liquid ammonia at 0° . Along *AB* the system is univariant, containing solid ammonium trinitride, saturated solution, and vapor. At *B* the solid phase disappears, or reappears, according as ammonia is being introduced into the system or withdrawn from it. This point therefore lies on the solubility curve. From the concentration of

the system it is apparent that at 0° liquid ammonia dissolves very nearly its own weight of ammonium trinitride. Along BC the system is bivariant, containing dilute solution and vapor.

The curve $ODEFGH$, which is the isotherm obtained at the boiling point of liquid ammonia (under a corrected barometric pressure of 730–742 cm., or about -33°), is composed of five parts. Along OD the system is bivariant, containing solid ammonium trinitride and vapor. At -33° ammonia begins to be absorbed by ammonium trinitride at a pressure of

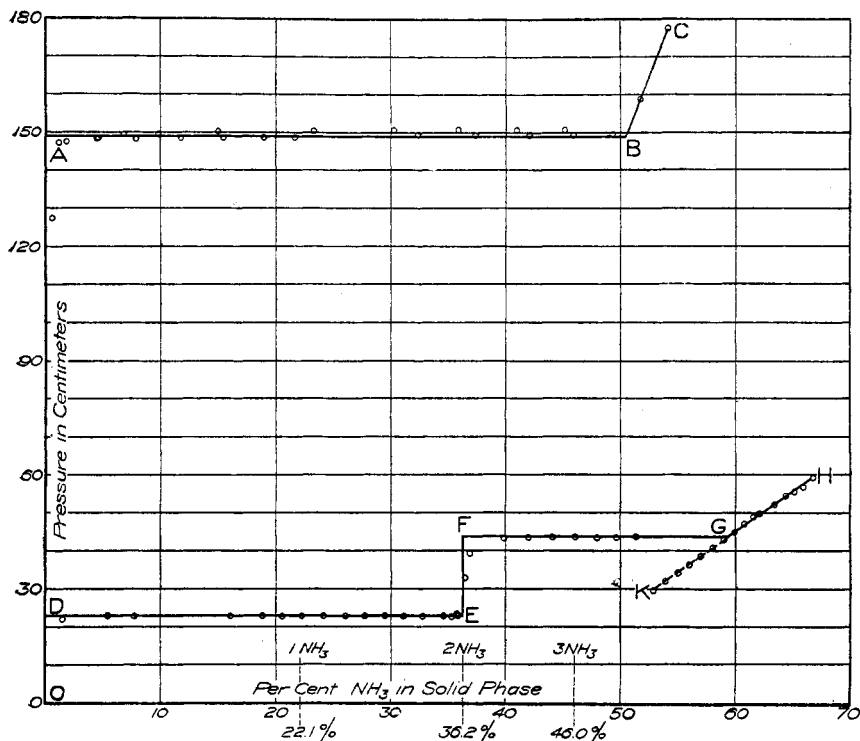


Fig. 2.

about 22.8 cm. This is the dissociation pressure of the diammonate, $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, at -33° . Along DE the system is univariant, containing solid ammonium trinitride, solid diammonate, and vapor. At E the solid phase is composed exclusively of the diammonate, which is a beautifully crystalline, colorless substance that has been repeatedly obtained by the authors in the form of "clear, somewhat elongated plates, that appear to be neither regular nor tetragonal."¹ In withdrawing

¹ The crystals were thus briefly characterized by Professor A. C. Gill of the Department of Geology of this University, to whom the authors wish to express their gratitude for his interest and assistance in the work.

ammonia from the system at *E* it was several times noted that certain small portions of the solid mass, particularly those attached to the walls of the cell, gave place to droplets of a metastable liquid, perhaps a supersaturated solution of the ammonious salt. These drops persisted at times until the point *D* was nearly reached. Along *EF* the system is bivariant, containing solid diammonate and vapor. In the region of this branch of the curve, it was found almost impossible to reach complete equilibrium in any reasonable length of time, probably owing to the presence of at least traces of saturated solution. Along *FG* the system is univariant, containing the diammonate, saturated solution, and vapor. The pressure of the saturated solution was found to be about 43.7 cm. at -33° . At *G* the solid phase disappears as more ammonia is introduced, and under normal conditions reappears as ammonia is withdrawn from the system. From the abscissa of this point, which lies on the solubility curve, it may readily be calculated that at -33° one gram of liquid ammonia dissolves very nearly seven-tenths of a gram of ammonium trinitride. In most of the experiments points were obtained along *FG* throughout its entire length. In the experiment of which the details are here given, however, the ammonia was withdrawn with considerable care in order to explore *GK*, the metastable prolongation of *GH*, as far as possible. Along *GH* the system is bivariant, containing dilute solution and vapor. Along *GK* it contains supersaturated solution and vapor. In withdrawing ammonia from the system after Observation 16, Table II, had been made, it was noted that a considerable quantity of a solid phase suddenly appeared, while the pressure at once rose to that of the saturated solution.

From the character of the isotherms studied it is apparent that ammonium trinitride forms with ammonia one addition product, the diammonate, $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, which, although stable at -33° , is incapable of existence at 0° . The inversion point must therefore lie between these temperatures. In the attempt to locate this point more definitely, two preliminary series of pressure-temperature measurements were conducted over a range of temperatures extending from -80° to $+20^{\circ}$. In the first of these series a sample of ammonium trinitride weighing 0.5491 gram was employed. Five experiments were performed, in which, respectively, about 100, 200, 300, 400, and 500 cc. of ammonia were present in the system. In the four experiments of the second series, 0.5334 gram of ammonium trinitride, and respectively about 100, 200, 300, and 400 cc. of ammonia were employed.

As a result of this study the course of three curves was approximately determined. Along the first of these coexist solid diammonate, saturated solution, and vapor; along the second, solid diammonate, solid ammonium trinitride, and vapor; along the third, solid ammonium trinitride, saturated solution, and vapor. These curves intersect in a quadruple point,

the inversion point of the diammonate, at which all four of the phases, solid diammonate, solid ammonium trinitride, saturated solution, and vapor, constituting an invariant system, coexist in equilibrium. This point was located in the neighborhood of -9° . The apparatus used in this work was the same as that used in the study of the isotherms, and was not well adapted for vigorous stirring of the system, and hence for the rapid attainment of equilibrium desirable in pressure-temperature work. Further details of these preliminary experiments need not be presented here, in view of the fact that Mr. Fritz Friedrichs of this laboratory has recently completed a thorough study of the system ammonium trinitride, ammonia over a wide range of temperature, pressure, and concentration. He has not only determined the course of numerous isotherms, and of the pressure-temperature curves, but also that of the solubility curve, establishing the existence of a monammonate, a diammonate, and a higher compound, probably the tetrammonate. Mr. Friedrichs has also completed a similar study of the two-component systems hydrazine, ammonia; ammonium bromide, ammonia; mercuric chloride, ammonia. Mr. L. J. Urich has completed an investigation of the system ammonium iodide, ammonia, and has made a comparative study of the 0° isotherms of a number of ammonium salts with ammonia. Among the other systems that have been investigated from the viewpoint of the phase rule within the past three years by different workers in this laboratory are: NH_4Cl , NH_3 ; $(\text{NH}_4)_2\text{SO}_4$, NH_3 ; NH_4SCN , NH_3 ; NH_4ClO_4 , NH_3 ; CuCl_2 , NH_3 ; CuSO_4 , NH_3 ; $\text{Cu}(\text{NO}_3)_2$, NH_3 ; CuSCN , NH_3 ; AgCl , NH_3 ; AgNO_3 , NH_3 ; AgN_3 , NH_3 ; CaCl_2 , NH_3 ; $\text{Ba}(\text{N}_3)_2$, NH_3 . The results of these investigations, as well as of others now in progress, in which hydrogen chloride or sulfur dioxide has been taken as the volatil component in place of ammonia, will be published in the near future. In all of this work greatly improved apparatus of the general type described in the present article has been employed. Sixteen of these pieces of apparatus have been constructed and are now in almost continuous operation. The chief object of the entire research is the accumulation of data in connection with numerous binary systems, chiefly those with one volatil component, with a view to throwing more light upon the nature of auxiliary valence, and upon the structure of addition products in general.

Several extensive investigations upon the ammonates have been published within the past few months. Peters¹ has studied the ammonates of 120 different salts from the viewpoint of the Werner theory of valence. F. Ephraim² has compared the dissociation temperatures of a series of ammonates of the general type $\text{Me}^n\text{Cl}_2.6\text{NH}_3$. In one of his later articles³

¹ *Z. anorg. Chem.*, **77**, 137-90 (1912).

² *Ber.*, **45**, 1322-31 (1912).

³ *Z. phys. Chem.*, **81**, 513 (1912).

Ephraim calls attention to what he considers to be a fundamental distinction between the hydrates and the ammonates, namely that the vapor-pressure curves of the hydrates show transition and inversion points, while those of the ammonates do not. He also states that while the hydrates have definite fields of existence, the ammonates have not, and explains this on the supposition that saturated solutions of the ammonates are not formed. All of these conclusions concerning the ammonates are in direct contradiction with the classical researches of Roozeboom¹ upon the system NH_4Br , NH_3 , and with the results obtained in this laboratory during the past three years. As pointed out by Mr. Friedrichs,² the ammonates studied by Ephraim happen to be, for the most part, insoluble in liquid ammonia, as shown by the work of Franklin and Kraus.³ These insoluble ammonates, which indeed under ordinary conditions do not show transition or inversion points, do not have definitely bounded fields of existence, and do not yield saturated solutions, have been compared by Ephraim with soluble hydrates, and an erroneous generalization, covering both soluble and insoluble ammonates, has been formulated.

Summary.

In the present investigation it has been shown:

(1) That ammonium trinitride, unlike ammonium chloride,⁴ ammonium bromide,⁵ and ammonium iodide,⁴ forms a diammonate, with the formula $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, obtained in the form of clear, colorless, somewhat elongated plates, that appear to be neither regular nor tetragonal.

(2) That the diammonate is stable at -33° , showing a dissociation pressure of about 22.8 cm. at this temperature. It is not stable at 0° , the inversion point being located at about -9° .

(3) That one gram of liquid ammonia will dissolve seven-tenths gram of ammonium trinitride at -33° , and one gram at 0° . The vapor pressure of the saturated solution at these two temperatures is respectively 43.7 and 149 cm.

CORNELL UNIVERSITY, ITHACA, N. Y.

STUDIES ON OSMOSIS.

BY C. FERDINAND NELSON.

Received April 1, 1913.

Introduction.

The exact nature of osmosis and of osmotic phenomena has engaged the attention of scientists for over a century. During this time many

¹ *Rec. trav. chim.*, 4, 361 (1885); *Z. physik. Chem.*, 2, 460 (1888).

² "Ueber die Natur der Nebervalenzen. Bemerkungen zur Abhandlung des Herrn Fritz Ephraim." *Z. physik. Chem.*, 82, (1913).

³ *Am. Chem. J.*, 20, 820-36 (1898).

⁴ Troost, *Compt. rend.*, 88, 578 (1879).

⁵ Troost, *Ibid.*, 92, 715 (1881); Roozeboom, *loc. cit.*