A STUDY OF THE KINETICS OF THE CHLORAMINE-AMMONIA AND
CHLORAMINE-HYDRAZINE REACTIONS IN LIQUID AMMONIA

DISSERTATION

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By

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A handwritten signature in cursive script, appearing to read "Jack Thoburn", is written over a horizontal line.

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INTRODUCTION

Industrial Significance of Hydrazine

The rise of hydrazine from a laboratory reagent to production on an industrial scale since the beginning of the Second World War derives from the discovery in Germany that anhydrous hydrazine, in the presence of strong oxidizing agents such as hydrogen peroxide, fuming nitric acid, or liquid oxygen constitutes a fuel that is far superior to any of the hydrocarbon fuels for use in missiles.¹ Its use² in synthesis, in pesticides, and bacteriocides, in antitubercular drugs, in defoliation sprays, and the challenging prospect of new uses account for its rapid rise to prominence as an industrial chemical. With the growth of production facilities, the remarkable drop in price³ has opened an economic pathway to further uses.

The history of the study of so promising a substance assumes a timely interest that superimposes itself upon the permanent and enduring interest that initially directs inquiring minds into problems of which the solution has

¹ L. F. Audrieth and B. A. Ogg, The Chemistry of Hydrazine (New York, John Wiley and Sons, Inc., 1951), p. 31.

² C. G. Clark, Hydrazine (Baltimore, Matheson Chemical Corporation, 1953), pp. 92-105.

³ Hans Zimmer, "Neuerer Entwicklungen auf dem Gebiet der Hydrazinchemie," Chemiker Zeitung, Vol. 79 (Sept., 1955), pp. 599-605.

no foreseen commercial importance. Attention is directed to the activity of early investigators.

History of the Raschig Synthesis of Hydrazine

Working with the substance called "hydrazine" by Emil Fischer⁴ Curtius prepared some of its salts and succeeded in obtaining not only an aqueous solution of the free base,⁵ but later the monohydrate.⁶

F. Raschig⁷ describes the growth of understanding of the reactions involved in hydrazine synthesis from chloramine and ammonia in aqueous solution containing fixed base. He begins with the observation by Johannes Thiele⁸ that a mixture of hypochlorite and excess ammonia gives rise to the evolution of gaseous nitrogen and that the solution has both oxidizing and reducing properties.

⁴ Emil Fischer, "Ueber aromatische Hydrazinverbindungen," Berichte der deutschen Chemischen Gesellschaft, Vol. 8 (April, 1875), pp. 589-594.

⁵ Theodore Curtius, "Ueber das Diamid (Hydrazin)," Berichte der deutschen Chemischen Gesellschaft, Vol. 20 (May, 1887), pp. 1632-1634.

⁶ Theodore Curtius and R. Jay, "Ueber das Hydrazin," Journal für Praktische Chemie, Vol. 39 (2) (Jan., 1889), pp. 27-58.

⁷ F. Raschig, Schwefel- und Stickstoffstudien (Leipzig-Berlin, Verlag Chemie, G.m.b.H., 1924), pp. 50-78.

⁸ Johannes Thiele, "Notiz über die Einwirkung von Ammoniak auf Hypochlorite," Justus Liebigs Annalen der Chemie, Vol. 273 (1893), pp. 160-163.

He points out the failure of Cross and Bevan⁹ properly to identify chloramine as one of the intermediates in the reaction, though they recognized its presence by its odor and volatility. He gives the stoichiometry of the overall reaction between chloramine and ammonia¹⁰ as

which encompasses both the formation and destruction of hydrazine. He describes his numerous experiments with the reaction mixture, coming to the experiment wherein he isolated hydrazine as the benzalazine, and finally to that wherein he discovered the conditions for formation of hydrazine by the now famous synthesis bearing his name.¹¹ He observed higher yields of hydrazine at higher temperatures, and sought both positive and negative catalysts to enhance the speed of the hydrazine forming reaction and to decrease the speed of the decomposition reaction, trying salts of metals, simple organic molecules such as formaldehyde and, finally, in 1906, sugar, albumin and glue, the latter being the most effective in decreasing the rate of decomposition.¹² He arrived at three of the four generally accepted equations involved in the

⁹ C. F. Cross and E. J. Bevan, "The Interaction of Hypochlorites and Ammonium Salts. Ammonium Hypochlorite," Proceedings of the Chemical Society (London) Vol. 6 (Feb. 1890), pp. 22-24.

¹⁰ F. Raschig, op. cit., p. 60

¹¹ Ibid., pp. 62-67.

¹² Ibid., p. 67.

the synthesis (2), (3), and (1).

His equation for the overall reaction, equation (1), is correct, but his separate expression for hydrazine destruction,¹³ equation (5),

is different from (4). Equations (3) and (4), if ammonia is used as the base, add to (1), whereas equations (4) and (5) do not.

Joyner¹⁴ noted that Raschig's equation for the production of nitrogen, equation (1), in view of the reducing properties of hydrazine, probably occurred in accordance with equation (4) through the intermediate, hydrazine, rather than by direct action of chloramine on ammonia. He studied effects of glue, ammonium chloride, added hydrazine, and ammonia to hypochlorite ratio on the yield of hydrazine in the Raschig synthesis. He interpreted the action of small quantities of glue in increasing the yield of hydrazine as due to the favorable effect on the formation reaction caused by the adsorption of the reactant, ammonia, on the particles of glue. Though he failed to

¹³ Ibid., p. 62.

¹⁴ R. A. Joyner, "Preparation of Hydrazine by Raschig's Method," Journal of the Chemical Society, (London), Vol. 123 (1923), pp. 1114-1121.

understand the action of the glue, he produced much work which has been duplicated by recent investigators. He did not propose a kinetic interpretation but was satisfied with the practical aspect of his results. He studied the combined effect of the formation and decomposition reactions in competition.

Bodenstein¹⁵ established the role of glue in complexing and effectively removing the heavy metal ions, especially cupric ion, which serve as positive catalysts for the decomposition reaction. This was shown in kinetic studies through the use of purified reagents to which traces (Cu^{++} 10^{-7} to 10^{-6} M/ml.) of the ions were added. He measured the kinetics of the summation reaction, equation (1)

and found it to be first order with respect to both chloramine and ammonia, little catalyzed by copper ion, and possessed of a high temperature coefficient. He followed nitrogen evolution and chloramine consumption at successive time intervals and computed concentrations of the other reactants. He worked with relatively dilute ammonia solutions under concentration conditions unfavorable to large hydrazine yields. He proposed two mechanisms

¹⁵ Max Bodenstein, "Monochloramin und Hydrazin. II. Bildung von Hydrazin und Zersetzung von Monochloramin in ammoniakalischer Lösung," Zeitschrift für Physikalische Chemie, Vol. 139A (1928), pp. 397-415.

for the oxidation of ammonia, one through the intermediate, hydroxyl amine, and one through hydrazine, though he favored the latter. He wrote equations (3) and (4) and their sum, equation (1). Like Joyner, he dealt with both reactions in competition. Neither he nor succeeding workers isolated and studied the formation reaction separately from the decomposition reaction. This approach was initiated by Hurley¹⁶ and continued and enlarged over a wide temperature range in the present work.

Studies of the Oxidation of Hydrazine in Aqueous Solution

The decomposition of hydrazine in aqueous solution by the action of various oxidizing agents has been investigated by A. W. Browne, an early paper appearing in 1905.¹⁷ A more recent paper by Kirke and Browne¹⁸ appeared in 1928. It deals with one- and two-electron

¹⁶ Forrest Reyburn Hurley, "Studies in Nitrogen Chemistry," Ph.D. dissertation, The Ohio State University, 1954, pp. 12-82.

¹⁷ A. W. Browne, "A New Synthesis of Hydronitric Acid," Journal of the American Chemical Society, Vol. 27 (May, 1905), pp. 551-555.

¹⁸ R. E. Kirke and A. W. Browne, "Oxidation of Hydrazine. VIII. Mono-Deelectronators and Di-deelectronators," Journal of the American Chemical Society, Vol. 50 (Feb., 1928), pp. 337-347.

oxidation of hydrazine and proposes a mechanism for the attack on hydrazine. This paper carries an abundant list of references to hydrazine oxidation. The list is amplified in the book of Audrieth and Ogg¹⁹ wherein a more general discussion of hydrazine oxidation is available. A paper by Higginson, Sutton, and Wright²⁰ brings the subject of one- and two-electron oxidation of hydrazine up to date and the work by Higginson and Sutton²¹ puts to test the mechanism of Kirke and Browne by the use of isotopically marked hydrazine. Their results lead them to propose free radical mechanisms for the oxidation in which Cahn and Powell,²² working independently on a similar study, concur. Additional references are available in the latter article.

¹⁹ L. F. Audrieth and B. A. Ogg, op. cit., pp. 148-152.

²⁰ W. C. E. Higginson, D. Sutton, and P. Wright, "The Oxidation of Hydrazine in Aqueous Solution. Part. I. The Nature of 1- and 2-Electron-transfer Reactions, with Particular Reference to the Oxidation of Hydrazine," Journal of the Chemical Society (London), Vol. 282 (1953), pp. 1380-1386.

²¹ W. C. E. Higginson and D. Sutton, "The Oxidation of Hydrazine in Aqueous Solution. Part II. The Use of ¹⁵N as a Tracer in the Oxidation of Hydrazine," Journal of the Chemical Society (London) Vol. 287 (1953), pp. 1402-1406.

²² J. W. Cahn and R. E. Powell, "Oxidation of Hydrazine in Solution," Journal of the American Chemical Society, Vol. 76 (May 5, 1954), pp. 2568-2572.

Synthesis of Hydrazine in Liquid Ammonia

A recent development in the history of the synthesis of hydrazine appeared in 1951 when Mattair and Sisler²³ announced the gas phase synthesis of chloramine from chlorine and ammonia followed by the reaction of the resultant chloramine when condensed in anhydrous ammonia, slowly, to form hydrazine according to the equations

Further studies were reported revealing yield reducing reactions both in the gas phase formation of chloramine²⁴

and in the liquid phase formation of hydrazine,²⁵ in which hydrazine is oxidized by excess chloramine to nitrogen according to the proposed equation

²³ Robert Mattair and H. H. Sisler, "The Production of Hydrazine by the Reaction of Chlorine with Anhydrous Ammonia," Journal of the American Chemical Society, Vol. 73 (April 10, 1951), pp. 1619-1622.

²⁴ H. H. Sisler, F. T. Neth, R. S. Drago, and Doyal Yaney, "The Synthesis of Chloramine by the Ammonia-Chlorine Reaction in the Gas Phase," Journal of the American Chemical Society, Vol. 76 (Aug. 5, 1954), pp. 3906-3909.

²⁵ H. H. Sisler, F. T. Neth, and F. R. Hurley, "The Chloramine-Ammonia Reaction in Liquid Ammonia," Journal of the American Chemical Society, Vol. 76 (Aug. 5, 1954), pp. 3909-3911.

Proposed Mechanisms for the Formation of Hydrazine

In an effort better to understand the Raschig synthesis of hydrazine, a number of chemists proposed mechanisms for the reaction and these can be extended to the synthesis in anhydrous ammonia. Audrieth, Colton, and Jones²⁶ proposed a mechanism wherein chloramine yields the chloramide ion, NHCl^- , which in turn breaks down to the α -imide molecule, NH . According to this mechanism the latter species adds to ammonia to form an intermediate which rearranges to hydrazine. They also applied this mechanism to the formation of hydrazine from t-butyl hypochlorite and ammonia. Audrieth and Diamond²⁷ extended it to the preparation of N-substituted hydrazines obtained in a modification of the Raschig synthesis. Colton, Jones and Audrieth²⁸ explained the formation of hydrazine from urea and t-butyl hypochlorite by a

²⁶ L. F. Audrieth, Ervin Colton, and M. M. Jones, "Formation of Hydrazine from t-Butyl Hypochlorite and Ammonia," Journal of the American Chemical Society, Vol. 76 (March 5, 1954), pp. 1428-1431.

²⁷ L. F. Audrieth and L. H. Diamond, "Preparation of N-Substituted Hydrazines by Modification of the Raschig Synthesis," Journal of the American Chemical Society, Vol. 76 (Oct. 5, 1954), pp. 4869-4871.

²⁸ Ervin Colton, M. M. Jones, and L. F. Audrieth, "The Preparation of Hydrazine from Urea and t-Butyl Hypochlorite," Journal of the American Chemical Society, Vol. 76 (May 5, 1954), pp. 2572-2574.

variation of the mechanisms. Jander,^{29,30,31} in a series of articles put forth evidence supporting the mechanism of Audrieth and co-workers. Cahn and Powell³² examined the yield data of the Raschig synthesis. Guided by the kinetic studies of Bodenstein³³ on the summation reaction, equation (1), they assumed bimolecular reaction mechanisms both for the formation and decomposition reactions and obtained close agreement with the experimental work of Joyner.³⁴ For the formation reaction they suggested a bimolecular displacement reaction,

Drago and Sisler³⁵ introduced evidence from their studies in liquid ammonia sustaining the Bodenstein, Cahn, and Powell mechanism for hydrazine formation,

²⁹ Jochen Jander, "Ueber Lösungen von Chloramin in flüssigem Ammoniak," Zeitschrift für anorganische und allgemeine Chemie, Vol. 280 (Sept., 1955), pp. 264-275.

³⁰ Jochen Jander, "Zum Verständnis der Chemie der Chlor-Stickstoff- und Chlor-Sauerstoff-Verbindungen," ibid., pp. 276-283.

³¹ Jochen Jander, "Ein Beitrag zur Kenntnis des Monochloramins," Die Naturwissenschaften, Vol. 42 (April, 1955), pp. 178-179.

³² J. W. Cahn and R. E. Powell, "The Raschig Synthesis of Hydrazine," Journal of the American Chemical Society, Vol. 76 (May 5, 1954), pp. 2565-2567.

³³ Max Bodenstein, op. cit.

³⁴ R. A. Joyner, op. cit.

³⁵ R. S. Drago and H. H. Sisler, "The Effect of Hydroxide and Ammonium Ions on the Reaction of Chloramine with Aqueous Ammonia," Journal of the American Chemical Society, Vol. 77 (June 20, 1955), pp. 3191-3194.

most significant being the isolation, in the case of the attack of chloramine on a trialkyl amine, of the intermediate quaternary hydrazinium salt $R_1R_2R_3NH_2^+Cl^-$.

Wiberg and Schmidt³⁶ proposed that the presence of water is essential to the Raschig or Raschig-like synthesis and asserted that the active oxidizing agent is hypochlorous acid rather than chloramine. Jones, Audrieth, and Colton³⁷ reported spectrophotometric studies which they interpreted to indicate that hypochlorous acid is not an intermediate in the process.

Proposed Mechanisms for the Oxidation of Hydrazine

Equations for the decomposition reaction of hydrazine were usually offered by investigators of its synthesis. Joyner³⁸ and Bodenstein³⁹ both gave equation (9) for the oxidation by chloramine.

³⁶ Egon Wiberg and Max Schmidt, "Über de Reaktionsmechanismus der Raschigschen Hydrazinsynthese," Zeitschrift für Naturforschung, Vol. 66 (1951), p. 336.

³⁷ M. M. Jones, L. F. Audrieth, and Ervin Colton, "Studies on the Raschig Synthesis of Hydrazine: The Reaction between Aqueous Chloramine and Ammonia Solutions," Journal of the American Chemical Society, Vol. 77 (May 20, 1955), pp. 2701-2703.

³⁸ R. A. Joyner, op. cit.

³⁹ Max Bodenstein, op. cit.

The Cahn, Powell, Bodenstein^{40,41} mechanism for the decomposition reaction assumed it to be bimolecular. As pointed out above, the assumption led to the proper yield data for the Raschig synthesis. In this work the authors did not attempt to define the intermediates in the oxidation.

The three mechanisms of Kirke and Browne⁴² are proposed to account for the accumulated experience of a number of investigators concerning the oxidation of hydrazine in aqueous solution.⁴³ Depending on conditions, the products are nitrogen, nitrogen and ammonia, or hydrazoic acid and ammonia. Corresponding intermediates suggested are NH_2NH , NH_2N , and $\text{NH}=\text{NH}$, respectively.

These mechanisms fail to account for the distribution of isotopic nitrogen from marked hydrazine, but the almost identical mechanisms proposed by the

⁴⁰ J. W. Cahn and R. E. Powell, "The Raschig Synthesis of Hydrazine," Journal of the American Chemical Society, Vol. 76 (May 5, 1954), pp. 2565-2567

⁴¹ Max Bodenstein, op. cit.

⁴² R. E. Kirke and A. W. Browne, op. cit.

⁴³ See paragraphs above headed "Oxidation of Hydrazine in Aqueous Solution."

investigators, Cahn and Powell,⁴⁴ Higginson, Sutton, and Wright⁴⁵ and Higginson and Sutton,⁴⁶ though quite different from that of Kirke and Browne do account for this distribution under the various conditions of oxidation in aqueous solution. They presume a free radical mechanism in acid solution involving the formation of the NH_2NH radical. This leads through tetrazane and triazene, with appropriate tautomerization, to nitrogen and ammonia. The 50% randomization of nitrogen predicted is observed. In basic solution they propose the formation of the $\text{HN}=\text{NH}$ radical. This is oxidized rapidly without randomization of isotopic nitrogen.

Statement of the Problem

Though extensive investigation of the Raschig synthesis had been reported in the literature, a new approach to the subject was desirable, since in all cases the studies that had been made were either in the nature of yield measurements, or, if kinetic, were of studies made on the sum of all the reactions involved, as expressed by the summation reaction, equation (1). The reactions, individually, had not been studied.

⁴⁴ J. W. Cahn and R. E. Powell, "Oxidation of Hydrazine in Solution," Journal of the American Chemical Society, Vol. 76 (May 5, 1954), pp. 2568-2572.

⁴⁵ W. C. E. Higginson, D. Sutton, and P. Wright, op. cit.

⁴⁶ W. C. E. Higginson and D. Sutton, op. cit.

A kinetic study was to be made, in liquid ammonia, of the reaction of chloramine and ammonia to form hydrazine and ammonium chloride, and of the reaction of chloramine with hydrazine to form nitrogen and ammonium chloride. The former reaction shall be designated as the formation reaction. It proceeds according to the equation:

The latter shall be designated as the decomposition reaction. It was presumed to proceed according to the following equation:

It was planned that the two reactions would be isolated in as far as possible by selecting conditions of temperature and concentration such as to emphasize one reaction and suppress the other as desired.

Because the only significantly ionized substance in the reaction mixture is the reaction product, ammonium chloride, the progress of the reaction would be followed conductimetrically. The concentration of ammonium chloride would be taken as a measure of the extent of the reaction.

In this manner it was hoped that the formation reaction could be studied, that its molecularity and order with respect to the reactants could be observed, and its

specific reaction rates measured at several temperatures. From the latter measurements it was expected that the energy and entropy of activation could be obtained. It was thought that a study of the kinetics might lead to a better understanding of the mechanism of the reaction. It might, at least, enable a choice to be made between several mechanisms currently offered for the formation reaction.

In a similar way it was hoped that the decomposition reaction could be understood. Because the decomposition reaction was thought to be effected through a complicated combination of reaction steps, it was expected that a continuous examination of the progress of the reaction might reveal peculiarities, such as an induction period, which would not be evidenced from yield data alone.

A knowledge of the kinetics of both reactions might produce an explanation of the manner in which high temperatures, low initial chloramine concentrations, and low ammonium chloride concentrations lead to higher yields of hydrazine.

The stoichiometry indicated in equation (9) had not been verified for the case of the reaction in liquid ammonia. Its confirmation was deemed necessary to justify methods used for computing concentrations of

reactants and products in the kinetic calculations.

In short, it was believed that a kinetics study might contribute to a more intimate understanding of the reactions involved in the synthesis of hydrazine.

EXPERIMENTAL PROCEDURES

Preparation and Purification of Reagents

Ammonia.- Verkamp anhydrous ammonia was obtained in cylinders containing fifty pounds of the liquid. Usually this liquid was heavily contaminated with a white solid, presumably ammonium carbamate, and some oil and grease from the valves of the cylinder. Gaseous ammonia was withdrawn from the cylinder held in an upright position. It was led through a glass wool plug and condensed (Figure 1) under a pressure of 150-250 mm. in a receiver in which it was to be used or stored. The receiver was immersed in a slurry of dry ice in a fifty volume-percent mixture of chloroform in carbon tetrachloride in order to effect the condensation.

Ammonium chloride.- Mallinckrodt analytical reagent grade ammonium chloride was used in the calibration of the conductivity cell. This was dried a minimum of two hours over sulfuric acid and stored over sulfuric acid in a weighing bottle. When ammonium chloride was to be added to a reaction mixture, however, that formed in the chloramine generator was used. It was thought to be freer of traces of impurities since it had never been recrystallized from water.

Fig.1
Ammonia Manometer
and Filter Tube

Chloramine.- Chloramine in liquid ammonia solution was obtained by condensing the gaseous chloramine and ammonia from a Sisler-Mattair generator.⁴⁷ Since such solutions were needed in the experimental work it was necessary to separate the chloramine from the ammonia. The large excesses of ammonia in the gas stream were useful in providing part of the solvent ammonia required. Additional liquid ammonia was placed in the receiver beforehand and cooled almost to its freezing point in order to slow down the decomposition of the chloramine. Since the solutions cannot be stored without deterioration, they were prepared as needed.

A description of the construction and a critical discussion of the operation of the Sisler-Mattair generator appears in the literature.⁴⁸ A diagram of the complete generator (Figure 2) with its accompanying descriptive legend and separate drawings of several of the component parts (Figures 3, 4, 5 and 6) are included in this manuscript.

A brief description of the operation of the generator may prove useful at this point. Chloramine is formed by

⁴⁷ Robert Mattair and H. H. Sisler, "The Production of Hydrazine by the Reaction of Chlorine with Anhydrous Ammonia," Journal of the American Chemical Society, Vol. 73 (April 10, 1951), pp. 1619-1622.

⁴⁸ H. H. Sisler, F. T. Neth, R. S. Drago, and Doyal Yaney, "The Synthesis of Chloramine by the Ammonia-Chlorine Reaction in the Gas Phase," Journal of the American Chemical Society, Vol. 76 (Aug. 5, 1954), pp. 3906-3909.

Figure 2

Chloramine Generator

- a. Chlorine container, non shatterable low pressure oxygen cylinder Type A-4 spec. 94-4036, internal volume 104 cu.in., half filled with liquid chlorine
- b. Reversed trap, empty
- c. Trap containing H_2SO_4
- d. Trap containing H_2SO_4
- e. Flow meter containing H_2SO_4 for measuring chlorine flow
- f. Flow meter containing methylsalicylate for measuring nitrogen flow
- g. Flow meter containing mercury for measuring ammonia flow
- h. Tower containing drierite to dry nitrogen
- i. Tower providing expansion volume for anhydrous ammonia
- j. Tube for mixing chlorine and nitrogen
- k. Plunger for clearing mixing tube jet of NH_4Cl
- l. Mixing jet
- m. Reactor tube
- n. Pyrex glass wool
- o. By-pass circuit
- p. Transfer tube
- q. Dewar
- r. Large pinch clamp
- s. Small pinch clamp
- t. Tube leading to hood
- u. Stopcocks

Chloramine Generator

Fig. 2

Mixing Jet
cross section
Fig.3

Mixing Jet

end view

Fig.4

Flow Meter

Fig. 5

Fig.6

the gas phase reaction of chlorine with ammonia. Approximately ten-fold excesses of ammonia are used to improve yields. Nitrogen is admixed as a diluting gas to retard the accumulation of an ammonium chloride plug in the mixing jets of the reactor. A plunger is also provided to remove the plug of ammonium chloride as it forms.

Flow meters (Figure 5) are introduced in the gas lines to make possible the monitoring of the gas volumes employed. The chlorine, diluted with nitrogen, is mixed with ammonia at a mixing jet. The gases react in a large tube and the resulting ammonium chloride is filtered off on a glass wool plug. Gaseous chloramine and ammonia are discharged from the generator.

Several alterations to the generator were made. The mixing jet (Figures 3 and 4) was redesigned in the interest of compactness. Chloramine yields are critically influenced by jet design. Quantitative measurements showed this design to produce chloramine in excess 85 percent yields. Methyl salicylate was substituted for sulfuric acid as the manometer fluid in the nitrogen flow meter. It is less troublesome in case of an overflow of the fluid. A by-pass circuit (Figure 6) was added to make it possible to run the generator to waste for a long enough period of time to obtain a reproducible effluent gas composition and then to divert it for a few minutes to a

receiver without interrupting the gas flow. In this manner a sample of predetermined size could be obtained.

The flow meters have interchangeable capillaries which are calibrated, in place, by means of the gas whose flow is to be subsequently monitored by the meter. The quantities of chlorine and ammonia used in calibration were measured by determining the loss in weight of a cylinder of the liquid after continuous withdrawal of the gas at constant flow meter reading for a period of an hour or so. The volumes of nitrogen used were measured by a wet test meter. The calibration data (Table 1) and calibration graphs (Figures 7, 8 and 9) of the three capillaries (Nos. 102, 101, and 4) are included.

Hydrazine.--The Matheson Company's anhydrous hydrazine as well as the Fairmount Chemical Company's anhydrous hydrazine, 95%, were employed in this work.

The principal objectionable impurity in each was water. This was removed by flake caustic. The hydrazine was allowed to stand over approximately one-fourth of its weight of flake caustic overnight in a sealed flask. The flask having a Standard Taper neck served also as the distilling bulb of the apparatus shown in Figure 10. The flask was put in place on the apparatus and the system carefully flushed with dry nitrogen. The pressure in the flask was reduced and it was allowed to fill again with dry nitrogen. The distilling flask was surrounded by a

Table 1 Calibration of Capillaries for Use in Flow Meters

Experiment number	Gas used	Capillary number	Manometer liquid	Time flowed	Average rise of liquid in right limb of flow meter-mm.	Gas flowed, units	Flow rate, units
2	Cl ₂	102	Conc. H ₂ SO ₄	1 hour	80	5.75 g.	5.75 g/hr.
3	Cl ₂	102	Conc. H ₂ SO ₄	1 hour	130	9.05 g.	9.05 g/hr.
4	Cl ₂	102	Conc. H ₂ SO ₄	1 hour	86	7.28 g.	7.28 g/hr.
5	Cl ₂	102	Conc. H ₂ SO ₄	1 hour	42	2.92 g.	2.92 g/hr.
6	Cl ₂	102	Conc. H ₂ SO ₄	37 min.	95	4.27 g.	6.92 g/hr.
7	N ₂	101	Methyl salicylate	1 hr. 1 min.	71	0.189 cu.ft.	0.183 cu.ft./hr.
9	N ₂	101	Methyl salicylate	1 hour	133	0.291 cu.ft.	0.291 cu.ft./hr.
11	N ₂	101	Methyl salicylate	1 hour	100	0.120 cu.ft.	0.120 cu.ft./hr.
13	N ₂	101	Methyl salicylate	1 hour	104	0.236 cu.ft.	0.236 cu.ft./hr.
15	N ₂	101	Methyl salicylate	1 hour	51	0.120 cu.ft.	0.120 cu.ft./hr.

Table 1 Calibration of Capillaries for Use in Flow Meters (cont.)

Experiment number	Gas used	Capillary number	Manometer liquid	Time flowed	Average rise of liquid in right limb of flow meter-mm.	Gas flowed, units	Flow rate, units
17	N ₂	101	Methyl salicylate	1 hour	76	0.170 cu.ft.	0.170 cu.ft./hr.
18	N ₂	101	Methyl salicylate	1 hr.1 min.	179	0.392 cu.ft.	0.385 cu.ft./hr.
8	NH ₃	4	Mercury	1 hour	19	14.65 g.	14.65 g./hr.
10	NH ₃	4	Mercury	1 hour	45	31.17 g.	31.17 g./hr.
12	NH ₃	4	Mercury	1 hr.1 min.	65	43.59 g.	42.86 g./hr.
14	NH ₃	4	Mercury	1 hour	80	49.16 g.	49.16 g./hr.
16	NH ₃	4	Mercury	1 hour	99	57.77 g.	57.77 g./hr.

CALIBRATION GRAPH OF CAPILLARY NUMBER 102 FOR USE IN FLOW METER

Fig. 7

CALIBRATION GRAPH OF CAPILLARY NUMBER 101 FOR USE IN
FLOW METER

Fig.8

CALIBRATION GRAPH OF CAPILLARY NUMBER 4 FOR USE IN
FLOW METER

Fig. 9

Hydrazine Still
 ($\frac{1}{2}$ size)
 Fig. 10

water bath and the pressure was pulled down to the point that hydrazine began to boil gently when the water bath was several degrees below sixty degrees C. The receiver was cooled in dry ice or liquid nitrogen. The neck of the receiver was not allowed to become cold as the hydrazine would have frozen there and sealed off the receiver. When sufficient hydrazine had been distilled the receiver was removed and capped. A serum bottle stopper was firmly attached to the sidearm of the receiving flask by a hose clamp. Samples were removed through this stopper by means of a hypodermic syringe using a number twenty-six needle. The flask was stored in a large desiccator away from the light.

Several precautions were observed during the operation: The apparatus was set up in a hood, safety shields were employed, the experimenter wore goggles, and great care was taken not to let the temperature of the water bath rise above sixty degrees C. A larger distilling flask than would seem necessary proved useful because of heavy foaming during distillation.

The purity of the hydrazine was tested by determining its freezing point in the cell shown in Figure 11. The stirrer was actuated by an electromagnet which was continually turned on and off by a motor drive switch. Liquid freezing more than half a degree below the accepted value of the freezing point was redistilled.

Fig.11

Apparatus

The apparatus employed in the conductivity measurements consisted of the conductivity cell, the conductivity bridge and auxillary capacitances, the thermostatic bath and its control equipment, and accessory glassware, baths, and manometers used in condensing and transferring ammonia and its solutions. Figure 12 provides a picture of the assembled apparatus with an accompanying legend that describes most of the parts.

Conductivity cell.— The conductivity cell was made in a design following that used by Hurley and described and illustrated in his dissertation.⁴⁹ A modification of this design is illustrated in Figure 13 of the present work.

Platinum electrodes in the form of wire loops rather than foil were used to minimize catalytic decomposition of hydrazine at their surfaces.

At -75°C . the cell leaked at the electrode seals due to the shrinking of the platinum away from the Pyrex glass envelope. A graded seal was substituted for the direct platinum-to-Pyrex glass union. It consisted of Corning Number 707 glass bonded to uranium glass, in that order, in going from the platinum wire electrode to the

⁴⁹ Forrest Reyburn Hurley, "Studies in Nitrogen Chemistry," Ph.D. dissertation, The Ohio State University, 1954, pp. 12-82.

Figure 12

Non-Scale Drawing of Apparatus Assembled for Making Rate Measurements

- A. Leeds and Northrup Company's number 40611-L1 micromax self recording potentiometer with control circuit
- B. Relay, 115 volts, 60 cycles per second
- C. Superior Electric Company's type 116 powerstat, primary voltage 115 volts, 50-60 cycles per second, maximum output of current, 7.5 amps.
- D. Central Scientific Company's knife heater, 500 watts, 115 volts
- E. Number 38 copper-constantan thermocouple encased in 3 mm. glass tube
- F. Ten parallel connected, individually switch operated 0.001 mfd. condensers
- G. General Radio Company's type 219-F decade condenser with decades of 0.01 mfd. and 0.10 mfd. condensers
- H. Industrial Instruments Incorporated's model RC16 conductivity bridge, 20 watts, 115 volts, 50-60 cycles per second, bridge frequency 60 or 1000 cycles per second
- I. Conductivity cell
- J. Mixing gas inlet tube for thermostatic bath
- K. Container for inner bath filled with acetone
- L. Container for intermediate bath filled with acetone
- M. Dewar container for outer bath filled with a slurry of dry ice in a 50 volume percent solution of chloroform in carbon tetrachloride
- N. Sodium hydroxide drying tube
- O. Manometer for ammonia gas
- P. Filter tube for ammonia gas
- Q. Cover for capillary₃₇ conductivity cell

Fig. 12

Apparatus Assembled for Making
Rate Measurements

Fig.13

Pyrex glass side arm. The side arm was sealed into the cell wall, giving a Pyrex-to-Pyrex glass union at this point where strain was likely to be great. However, these seals were not notably superior to the direct platinum-to-Pyrex glass seal because the large diameter platinum wire (B. and S. gauge No. 18) shrank considerably more than did the graded seal under the large temperature drops to which it was subjected. A smaller wire could have been used to advantage had not maximum rigidity of electrodes been necessary to maintain constant electrode spacing.

In order to facilitate measurements described in the section on the stoichiometry of the decomposition reaction, the electrodes were introduced high up on the body of the cell.

Suitable leads were made of B. and S. gauge number eighteen copper wires, to the cell ends of which a short nickel metal strip was spot welded. A five centimeter length of B. and S. gauge number twenty-eight platinum wire was spot welded to the other end of the nickel strip. Each lead was insulated by close fitting plastic tubing known as "spaghetti". The platinum tips on the leads do not amalgamate with the mercury used in the side arms of the cell. Though unshielded, the leads did not pick up induced voltages of sufficient magnitude to affect the balance point of the bridge.

Conductivity bridge and auxiliary capacitances.- The conductivity bridge employed was Industrial Instruments Incorporated's conductivity bridge, Model R.C. 16, designed to consume twenty watts and to operate on the 115 volt 60 cycle line. The internal oscillator of the bridge could be adjusted to oscillate at either 60 or 1000 cycles per second. All the measurements were made at 1000 cycles per second.

Auxiliary capacitances used were General Radio Company's type 219-F decade condenser with decades of 0.01 and 0.10 microfarad condensers, and a set of ten parallel connected, individually switch operated 0.001 microfarad condensers. These were employed to balance out capacity effects in the circuit.

Thermostatic bath.- In order to make rate measurements at several widely spaced temperature intervals, it was found useful to have a readily adjustable thermostatic bath (Figure 12). Rate measurements had been made⁵⁰ using liquid ammonia itself as a thermostating liquid, but these were at the normal boiling point only. There seem to be no commonly available, safe, relatively cheap, and convenient substances which give transition temperatures intermediate between the boiling point and the freezing

⁵⁰

Forrest Reyburn Hurley, ibid., pp. 12-43.

point of ammonia, the solvent chosen for the reaction.

Dry ice, which is a readily available thermostating substance, sublimates at a temperature which is about a degree below the freezing point of ammonia and is for that reason unsuitable for this use. However, it was found satisfactory when used as an external coolant to a bath which was internally but intermittently heated to maintain the temperature at some desired level.

The Leeds and Northrup Company's Micromax self recording potentiometer with control circuit was selected to control this heating because of its simplicity and dependability of operation, and its moderate, though adequate sensitivity of response. Though it does not react rapidly to temperature fluctuations, it was easily adjusted to control at any temperature within the range -33° to -77°C . in which ammonia is normally a liquid. The number thirty-eight copper-constantan thermocouple provides a means of measuring and recording the temperature and also of providing the signal to which the control circuit of the micromax responds through a relay to operate the heater.

A four-liter dewar was used as the outer bath and was filled with a heavy slurry of dry ice in a fifty volume-percent solution of chloroform in a carbon tetrachloride. A large test tube shaped vessel, 90x270 mm., was used as the inner bath container. A larger test tube shaped vessel, 120x280 mm., surrounding the smaller vessel, was

used as an intermediate bath container when there was a large temperature gradient between the inner and outer bath and a region of insulation was needed between them. The two tubes were concentrically mounted in the dewar (Figures 14 and 15) with wire gauze pads acting as spacers at their bottoms. They were each filled with acetone which remained clear and allowed a view of the conductivity cell and its contents even when an appreciable quantity of water had condensed in it from the atmosphere. The acetone was replaced daily to prevent the accumulation of an ice phase which would have plugged the mixing gas inlet tube.

The inner bath was stirred by a rapid stream of dry nitrogen introduced at the bottom through a J-shaped glass tube drawn out to a small tip. The conductivity cell was approximately centered in the bath. A teflon gasket (Figure 16) was used to hold the cell and the other components roughly in place. A 500 watt, 115 volt Cenco Immersion Knife Heater operating through a Powerstat was inserted in the bath beside the conductivity cell. The output of the heater was adjusted so that the heating half of the cycle lasted as long as the cooling half. A strip of wire gauze served as a separator between the heater and the cell. Rapid stirring was necessary to prevent the heater from warming the conductivity cell more than the rest of the bath. The cell was raised off the

-44-

Fig.14

Top View of Assembled Thermostatic Bath

Fig.15

Teflon Placement Gasket

Fig.16

bottom of the bath on a wire gauze pad.

The thermocouple, sheathed in a three millimeter glass tube filled with petroleum ether, was inserted deeply into the bath.

The performance of the bath was altogether satisfactory for these experiments. At a temperature setting of -75°C . with only a few degrees difference between the inner bath and outer bath temperatures, the temperature could be maintained constant within $\pm 0.45^{\circ}\text{C}$. even without the use of the intermediate bath. The intermediate bath was used at higher temperatures. At a setting of -38°C . the temperature was held within $\pm 1.1^{\circ}\text{C}$. In order to minimize the effect of these fluctuations, conductivity readings were always made at the same point in the cycle whenever there was time to wait for the cycle to change.

Since the "electronic eye" on the conductivity bridge would not properly focus during the heating half of the temperature cycle, it was convenient to take the readings just at the end of the heating half of the cycle. When readings were taken during the heating half of the cycle, it was necessary to shut off the entire control circuit for the time required to obtain them.

Accessory glassware.- Various accessory tubes, syphons, baths, and manometers were used in condensing and transferring ammonia and its solutions. Their use is indicated at appropriate points in the description of the

procedure for calibrating the conductivity cell and for making rate measurements. Figures indicating details of construction of this apparatus are inserted at these points and are referred to by number.

Calibration of the Conductivity Cell

Purpose of the calibration.- The quantitative knowledge of the progress of the reactions under study depends on the measurement of the ammonium chloride concentration in the reaction mixture at a given time. This measurement was made conductimetrically. The relationships between the concentration of ammonium chloride and the reciprocal resistance of the solution between electrodes at a given temperature was determined experimentally in the process of calibration, whereby weighed quantities of ammonium chloride were added to liquid ammonia to compose solutions of known volume. The resistance of these solutions was measured. Mixtures were prepared to correspond with the entire concentration range encountered in the experiments. Thus an isotherm of the reciprocal of the cell resistance vs. the concentration of ammonium chloride could be composed. A new isotherm was obtained for each temperature at which the cell was to be used. A family of isotherms was prepared for each cell employed since the geometry, and hence the calibration data, of no two cells was the same.

Calibration procedure.- The conductivity cell was cleaned by washing first with distilled water and then with acetone. The cell was dried by a stream of dry nitrogen. It was placed in the thermostat which was allowed to sink to the temperature of the cooling mixture to facilitate condensing ammonia within the cell. Ammonia was condensed in the cell as a rinse liquid in small quantities several times, and twice in quantities sufficient to fill it entirely. Each time the liquid was actively mixed by a stream of dry nitrogen and then discharged from the cell by dry nitrogen pressure. The vigor of the mixing was controlled by a capillary installed in the outlet from the nitrogen train and by fingering the outlet of the nitrogen by-pass line while carefully observing the rate of mixing. Overflow of the cell contents was thus avoided during mixing in most cases.

A fresh charge of ammonia was condensed in the cell and a stream of nitrogen sufficiently rapid to minimize thermal gradients was passed through the thermostating bath. The micromax circuits and the intermittent heater were turned on and the potentiometer circuit of the micromax balanced. The bath was allowed to reach operating temperature. The ammonia was mixed by a stream of dry nitrogen. If it was sufficiently pure to give a resistance reading of 200,000 to 800,000 ohms (equivalent of less than one milligram of ammonium chloride per 100 ml.

of solution) it was retained for use, otherwise, it was discharged and another tubeful was condensed. After the ammonia had attained bath temperature, the liquid volume in the cell was adjusted by condensing more ammonia in it or blowing out any surplus until the meniscus lay within the two volumetric lines on the neck of the cell. In subsequent operations losses of ammonia due to evaporation during mixing were not ordinarily made up, but instead, the volume was noted.

Ammonium chloride samples for the calibration were weighed by difference into the cell using a microspatula and a long stemmed funnel that reached just above the level of the ammonia in the neck of the cell. The funnel was inserted in the neck of the cell for only a few moments so that it would not cool, become covered with condensed moisture, and thereby retain small particles of ammonium chloride on its inner surface. Samples beginning in size in a few milligrams were used, and the sample size increased as the response of the cell to changes in concentration became less at higher concentrations. During any series of determinations it was customary to add the salt to the solution containing the preceding samples and to use the total of the sample weights as the measure of the dissolved material.

After the sample was introduced, the contents of the cell were mixed so actively by a stream of dry nitrogen

that any salt which might have adhered to the walls of the cell above the liquid was washed into the solution, and so that all the salt was dissolved and uniformly distributed throughout the solution. Uniform distribution was indicated by constant resistance readings after repeated mixings. Several minutes of actual mixing were divided into three or four intervals with resistance readings observed after each mixing. The readings were taken just after the intermittent heater went off, in order to get the readings as nearly as possible at the same temperature each time. The measurement of the concentration was extremely sensitive to temperature errors. In using the cell for rate measurements, where possible, the same procedure was used.

The volume of the solution was noted after each resistance reading.

Calibration data.— The calibration data are recorded in Table 2.

It was found that a plot of the logarithm of the reciprocal of the cell resistance gave a straight line graph when plotted against the logarithm of the ammonium chloride concentration. This observation is in accord with the discussion by Harned and Owen⁵¹ in which the

⁵¹ H. S. Harned and B. S. Owen, The Physical Chemistry of Electrolytic Solutions (2nd ed. rev.; New York, Reinhold Publishing Corporation, 1950), pp. 155-156.

Table 2 Calibration Data for Conductivity Cells:

Concentration of Ammonium Chloride in Liquid Ammonia vs. Reciprocal Resistance

Cell Number 1

Temperature -34.2

No.	Wt. dis- solved, NH ₄ Cl, grams	Volume of sol'n., liters	Conc. NH ₄ Cl moles/liter x 10 ³	Resistance reading, ohms	Reciprocal Resistance mhos x 10 ⁵
1	0.0047	0.07307	1.202	5,620	17.80
2	0.0098	0.07277	2.517	3,150	31.75
3	0.0159	0.07247	4.101	2,190	45.66
4A	0.0058	0.07307	1.483	4,620	21.65
4B	0.0058	0.07307	1.483	4,720	21.20
5	0.0128	0.07307	3.275	2,560	39.06
6	0.0194	0.07297	4.969	1,910	52.36
7	0.0321	0.07297	8.222	1,320	75.76
9	0.0373	0.07337	9.500	1,200	83.33
11	0.0059	0.07307	1.509	4,560	21.93
12	0.0115	0.07297	2.946	2,770	36.10
13	0.0203	0.07247	5.235	1,790	55.86
14	0.0285	0.07267	7.330	1,410	70.92
15	0.0373	0.07247	9.618	1,150	86.96
17	0.0062	0.07367	1.572	4,350	22.99
18	0.0103	0.07357	2.616	3,202	33.11
19	0.0160	0.07307	4.092	2,160	46.30
20	0.0208	0.07287	5.338	1,770	56.50
21	0.0280	0.07277	7.192	1,430	69.93
22	0.0371	0.07257	9.549	1,160	86.21
23	0.0045	0.07397	1.137	5,670	17.64
24	0.0099	0.07377	2.508	3,070	32.57

Table 2 Calibration Data for Conductivity Cells (cont.)

Cell Number 1

Temperature -34.2, cont.

No.	Wt. dis- solved, NH ₄ Cl, grams	Volume of sol'n., liters	Conc. NH ₄ Cl moles/liter x10 ³	Resistance reading, ohms	Reciprocal Resistance mhos x 10 ⁵
25	0.0248	0.07367	6.285	1,570	63.69
26	0.0335	0.07357	8.509	1,265	79.05
27	0.454	0.07357	11.526	1,030	97.09
28	0.0579	0.07347	14.727	860	116.28
29	0.0702	0.07317	17.931	745	134.23
30	0.0884	0.07307	22.608	642	155.76
31	0.0065	0.07367	1.649	4,350	22.99
32	0.0186	0.07337	4.739	1,930	51.81
33	0.0296	0.07307	7.572	1,390	71.94
34	0.0434	0.07307	11.102	1,058	94.52
35	0.0580	0.07277	14.896	862	116.01
36	0.0689	0.07247	17.776	760	131.58
37	0.0820	0.07447	20.585	687	145.56
38	0.0991	0.07437	24.902	597	167.50
39	0.1205	0.07437	30.281	520	192.31
40	0.1419	0.07417	35.756	463	215.98
41	0.0082	0.07417	2.065	3,680	27.17
42	0.0372	0.07407	9.383	1,190	84.03
43	0.0794	0.07357	20.171	690	144.93
44	0.1012	0.07357	25.703	587	170.36
45	0.1243	0.07347	31.618	507	197.24
46	0.1553	0.07347	39.513	435	229.88

Table 2 Calibration Data for Conductivity Cells (cont.)

Cell Number 2

Temperature -75°C.

No.	Wt. dis- solved, NH ₄ Cl, grams	Volume of sol'n., liters	Conc. NH ₄ Cl moles/liter x 10 ³	Resistance reading, ohms	Reciprocal Resistance mhos x 10 ⁵
47	0.0221	0.07485	5.518	2,800	35.71
48	0.0036	0.06858	.983	13,350	7.49
49	0.0204	0.07160	5.325	3,000	33.33
50	0.0376	0.07125	9.867	1,950	51.28
51	0.0082	0.07043	2.177	5,790	17.27
52	0.0190	0.07028	5.051	3,030	33.00
53	0.0430	0.07028	11.425	1,670	59.88
54	0.0791	0.07043	20.98	1,073	93.20
55	0.1346	0.07028	35.811	723	138.31
56	0.0052	0.07033	1.382	6,960	14.37
57	0.0167	0.07043	4.431	3,280	30.49
58	0.0417	0.07058	11.037	1,700	58.82
59	0.0915	0.07048	24.262	970	103.09
60	0.1632	0.07048	43.275	630	158.73
61	0.0147	0.07073	3.885	3,890	25.71
62	0.0701	0.07078	18.508	1,235	80.97
63	0.1133	0.07078	29.951	843	118.62
64	0.1830	0.07083	48.285	590	169.49
65	0.2425	0.07083	63.955	480	208.33
67	0.0144	0.07095	3.791	3,500	28.57
68	0.0243	0.07100	6.394	2,430	41.15
69	0.0330	0.07110	8.678	1,970	50.76
70	0.0736	0.07100	19.380	1,100	90.91
71	0.1037	0.07095	27.315	860	116.28
72	0.0088	0.06988	2.353	5,100	19.61

Table 2 Calibration Data for Conductivity Cells (cont.)

Cell Number 2

Temperature -75°C. , cont.

No.	Wt. dis- solved, NH_4Cl , grams	Volume of sol'n., liters	Conc. NH_4Cl moles/liter $\times 10^3$	Resistance reading, ohms	Reciprocal Resistance mhos $\times 10^5$
73	0.0343	0.07008	9.147	1,980	50.50
74	0.0738	0.06998	19.720	1,145	87.34
75	0.0946	0.06988	25.300	950	105.26

Table 2 Calibration Data for Conductivity Cells (cont.)

Cell Number 3

Temperature -75°C.

No.	Wt. dis- solved, NH ₄ Cl, grams	Volume of sol'n., liters	Conc. NH ₄ Cl moles/liter x 10 ³	Resistance reading, ohms	Reciprocal Resistance mhos x 10 ⁵
94	0.0135	0.07236	3.487	3,120	32.05
95	0.0349	0.07229	9.026	1,560	64.10
96	0.0769	0.07229	19.878	870	114.94
97	0.1216	0.07219	31.486	630	158.73
98	0.1597	0.07209	41.406	510	196.08
100	0.0056	0.07229	1.448	5,980	16.72
101	0.0157	0.07224	4.061	2,720	36.76
102	0.0300	0.07224	7.766	1,770	56.49
103	0.0656	0.07219	16.983	995	100.50
104	0.1089	0.07214	28.209	690	144.93
105	0.1574	0.07219	40.754	523	191.20
106	0.00044	0.07010	0.118	46,000	2.17
108	0.00075	0.07090	0.198	32,000	3.12
109	0.00090	0.07256	0.232	31,000	3.22
110	0.00060	0.07276	0.154	42,100	2.38
111	0.00233	0.07286	0.598	12,300	8.13
112	0.00120	0.07316	0.306	29,500	3.39
113	0.00225	0.07246	0.581	13,750	7.27
114	0.000885	0.07089	0.233	30,200	3.31

Table 2 Calibration Data for Conductivity Cells (cont.)

Cell Number 4

Temperature -75°C.

No.	Wt. dissolved, NH ₄ Cl, grams	Volume of sol'n., liters	Conc. NH ₄ Cl moles/liter x 10 ³	Resistance reading, ohms	Reciprocal Resistance mhos x 10 ⁵
115	0.0032	0.07089	0.843	9,670	10.34
116	0.0026	0.07139	0.681	12,000	8.33
117	0.0062	0.07129	1.625	5,780	17.30
118	0.0120	0.07124	3.148	3,480	28.73
119	0.0242	0.07109	6.362	2,080	48.08
120	0.0441	0.07104	11.603	1,320	75.75
121	0.0028	0.07219	0.724	11,920	8.38
122	0.0085	0.07209	2.204	4,720	21.20
123	0.0171	0.07209	4.433	2,690	31.17
124	0.0274	0.07199	7.113	1,930	51.81
125	0.0424	0.07199	11.008	1,380	72.46
126	0.0588	0.07189	15.287	1,082	92.42
128	0.0030	0.07234	0.776	12,180	8.21
129	0.0094	0.07234	2.428	4,770	20.96
130	0.0159	0.07229	4.111	3,030	33.00
131	0.0238	0.07224	6.160	2,220	45.04
132	0.0414	0.07219	10.722	1,427	70.08
133	0.0559	0.07209	14.496	1,150	86.96
134	0.0815	0.07209	21.126	861	116.14
135	0.1142	0.07209	29.602	664	150.60
136	0.0025	0.07239	0.645	15,600	6.41
137	0.0040	0.07232	1.034	9,580	10.43
138	0.0075	0.07229	1.939	5,750	17.39
139	0.0121	0.07224	3.131	3,720	26.88
140	0.0221	0.07219	5.722	2,360	42.37

Table 2 Calibration Data for Conductivity Cells (cont.)

Cell Number 4

Temperature -75°C., cont.

No.	Wt. dis- solved, NH ₄ Cl, grams	Volume of sol'n., liters	Conc. NH ₄ Cl moles/liter x 10 ³	Resistance reading, ohms,	Reciprocal Resistance mhos x 10 ⁵
141	0.0404	0.07214	10.465	1,480	67.57
142	0.0665	0.07214	17.230	1,010	99.01
143	0.0995	0.07214	25.783	764	130.89
144	0.1446	0.07209	37.495	570	175.44

Cell Number 4

Temperature -60°C.

145	0.0026	0.07209	0.674	9,400	10.64
146	0.0091	0.07209	2.359	3,210	31.15
147	0.0222	0.07209	5.755	1,650	60.61
148	0.0370	0.07149	9.674	1,160	86.21
149	0.0737	0.07139	19.297	700	142.85
150	0.1033	0.07109	27.163	545	183.48
151A	0.1564	0.07119	41.059	367	272.48
151B	0.1564	0.07074	41.320	400	250.00
152	0.0019	0.07306	0.486	11,250	8.89
153	0.0061	0.07296	1.562	4,020	24.88
154	0.0110	0.07276	2.825	2,510	39.84
155	0.0251	0.07236	6.484	1,325	75.47
156A	0.0564	0.07224	14.593	732	136.61
156B	0.0564	0.07069	14.913	852	117.37
157	0.0941	0.07049	24.952	585	1170.94
158	0.1233	0.07049	32.700	472	211.86
159	0.1553	0.07039	41.242	405	246.91
160	0.0015	0.07236	0.387	14,000	7.14

Table 2 Calibration Data for Conductivity Cells (cont.)

Cell Number 4

Temperature -60°C., cont.

No.	Wt. dis- solved, NH ₄ Cl, grams	Volume of sol'n., liters	Conc. NH ₄ Cl moles/liter x 10 ³	Resistance reading, ohms	Reciprocal Resistance mhos x 10 ⁵
161	0.0039	0.07224	1.009	6,780	14.75
162	0.0087	0.07214	2.253	3,570	28.01
163	0.0209	0.07199	5.427	1,825	54.79
164	0.0573	0.07179	14.918	855	116.95
165	0.0975	0.07169	25.420	572	174.82
166	0.1382	0.07139	36.183	445	224.72
167	0.1995	0.07139	52.233	335	298.51
168	0.0027	0.07236	0.698	9,950	10.05
169	0.0095	0.07224	2.458	3,400	29.41
170	0.0240	0.07199	6.230	1,650	60.61
171	0.0768	0.07189	19.968	692	144.50
172	0.1404	0.07189	33.885	468	213.68
173	0.1869	0.07186	48.608	356	280.90

Cell Number 4

Temperature -50°C

174	0.0016	0.07139	0.419	12,450	8.03
175	0.0042	0.07139	1.100	5,270	18.98
176	0.0082	0.07124	2.152	3,170	31.55
177	0.0133	0.07119	3.492	2,270	44.05
178	0.0249	0.07109	6.547	1,395	71.68
179	0.0433	0.07109	11.384	945	105.82
180	0.0660	0.07104	17.364	698	143.26
181	0.1076	0.07099	28.330	496	201.61

Table 2 Calibration Data for Conductivity Cells (cont.)

Cell Number 4

Temperature -50°C., cont.

No.	Wt. dis- solved, NH ₄ Cl, grams	Volume of sol'n., liters	Conc. NH ₄ Cl moles/liter x 10 ³	Resistance reading, ohms	Reciprocal Resistance mhos x 10 ⁵
182	0.1628	0.07099	42.863	361	277.00
183	0.0017	0.07209	0.441	12,220	8.18
184	0.0028	0.07199	0.726	7,990	12.52
185	0.0041	0.07199	1.064	6,070	16.47
186	0.0067	0.07179	0.174	4,050	24.69
187	0.0106	0.07159	2.767	2,770	36.10
188	0.0170	0.07149	4.445	1,920	52.08
189	0.0261	0.07149	6.825	1,367	73.15
190	0.0411	0.07139	10.761	980	102.04
191	0.0696	0.07139	18.222	662	151.05
192	0.1087	0.07129	28.500	477	209.64
193	0.1517	0.07119	39.830	370	270.27
194	0.0006	0.07236	0.155	35,700	2.80
195	0.0017	0.07229	0.440	13,400	7.46
196	0.0031	0.07209	0.803	7,800	12.82
197	0.0058	0.07199	1.506	4,400	22.73
198	0.0108	0.07159	2.819	2,650	37.74
199	0.0170	0.07139	4.450	1,870	53.48
200	0.0239	0.07139	6.257	1,440	69.44
201	0.0442	0.07139	11.572	913	109.52
202	0.0694	0.07129	18.194	655	152.67
203	0.0958	0.07119	25.153	513	194.93
204	0.1392	0.07109	36.598	390	256.41

Table 2 Calibration Data for Conductivity Cells (cont.)

Cell Number 4

Temperature -38°C.

No.	Wt. dis- solved, NH ₄ Cl, grams	Volume of sol'n., liters	Conc. NH ₄ Cl moles/liter x 10 ³	Resistance reading, ohms	Reciprocal Resistance mhos x 10 ⁵
205	0.0011	0.07244	0.284	14,450	6.92
206	0.0033	0.07234	0.853	5,530	18.08
207	0.0060	0.07214	1.554	3,430	29.15
208	0.0089	0.07199	2.311	2,600	38.46
209	0.0135	0.07184	3.512	1,900	52.63
210	0.0200	0.07149	5.229	1,415	70.67
211	0.0269	0.07129	7.053	1,135	88.11
212	0.0422	0.07114	11.088	818	122.25
213	0.0572	0.07109	15.040	655	152.67
214	0.0007	0.07209	0.182	30,000	3.33
215	0.0013	0.07189	0.338	14,370	6.96
216	0.0028	0.07129	0.734	6,810	14.68
217	0.0043	0.07109	1.131	4,710	21.23
218	0.0064	0.07104	1.684	3,420	29.24
219	0.0144	0.07099	3.791	1,815	55.10
220	0.0218	0.07084	5.751	1,327	75.36
221	0.0387	0.07074	10.225	872	114.68
222	0.0662	0.07064	17.515	578	173.01
223	0.0959	0.07049	25.429	443	225.73
224	0.1337	0.07029	35.552	347	288.18
225	0.0010	0.07219	0.259	15,350	6.51
226	0.0020	0.07179	0.521	8,730	11.45
227	0.0029	0.07149	0.758	6,430	15.55
228	0.0083	0.07139	2.173	2,770	36.10
229	0.0123	0.07129	3.225	2,050	48.78

Table 2 Calibration Data for Conductivity Cells (cont.)

Cell Number 4

Temperature -38°C. , cont.

No.	Wt. dis- solved, NH_4Cl , grams	Volume of sol'n., liters	Conc. NH_4Cl moles/liter $\times 10^3$	Resistance reading, ohms	Reciprocal Resistance mhos $\times 10^5$
230	0.0193	0.07119	5.067	1,445	69.20
231	0.0315	0.07104	8.287	1,010	99.01
232	0.0437	0.07089	11.522	797	125.47
233	0.0602	0.07074	15.906	627	159.49
234	0.0759	0.07069	20.067	530	188.68
235	0.0923	0.07059	24.439	457	218.82
236	0.1155	0.07059	30.582	387	258.40

Table 2 Calibration Data for Conductivity Cells (cont.)

Cell Number 5
Temperature -38°C .

No.	Wt. dis- solved, NH_4Cl , grams	Volume of sol'n., liters	Conc. NH_4Cl moles/liter $\times 10^3$	Resistance reading ohms	Reciprocal Resistance mhos $\times 10^5$
237	0.0018	0.07270	0.462	4,790	20.92
238	0.0072	0.07198	1.870	1,520	65.79
239	0.0144	0.07126	3.778	943	106.04
240	0.0218	0.07054	5.777	710	140.84
241	0.0297	0.06982	7.950	590	169.49
242	0.0403	0.06910	10.902	490	204.08
243	0.0582	0.06838	15.908	385	259.74
244	0.0900	0.06766	24.863	285	350.87
245	0.1344	0.06694	37.528	220	454.54

$$\log(\Lambda^0 - \Lambda) = n \log c + \text{constant} \quad (11)$$

was reported to apply to the conductances of a large number of electrolytes. The relationship leads to a straight line plot of slope, n , if Λ^0 is judiciously chosen.

Log-log graphical representations of the calibration data are provided in Figures 17-24 inclusive.

Measurement of Reaction Rate

Separation of the two reactions.— The procedure for making a measurement of the rate of reaction in the case of either the formation or decomposition reaction depends on the determination of the rate of formation of ammonium chloride, a product of either reaction. The rate measurement is made conductimetrically.

The equations proposed for the formation and decomposition reactions, as listed earlier, are

The stoichiometry of equation (9) was verified for the reaction in liquid ammonia in this work and is reported in the section on the stoichiometry of the decomposition reaction. According to these equations the rate of formation of ammonium chloride is equal to the rate of decomposition of chloramine in either case, whereas the rate of formation of ammonium chloride equals the rate of

CALIBRATION GRAPH FOR CONDUCTIVITY CELL

Fig.17

CALIBRATION GRAPH FOR CONDUCTIVITY CELL

Fig. 18

CALIBRATION GRAPH FOR CONDUCTIVITY CELL

Fig.19

CALIBRATION GRAPH FOR CONDUCTIVITY CELL

Fig. 20

Fig. 21

CALIBRATION GRAPH FOR CONDUCTIVITY CELL

Fig. 22

CALIBRATION GRAPH FOR CONDUCTIVITY CELL

Fig. 23

CALIBRATION GRAPH FOR CONDUCTIVITY CELL

Fig.24

formation of hydrazine in the first case or twice the rate of decomposition of hydrazine in the second case.

It should be noted that the ammonia acts as a reactant as well as the solvent in the formation reaction.

Isolation of the reactions, one from the other, insofar as it can be achieved, depends on a choice of the experimental conditions. These in turn govern the experimental procedure. If the composition of the reaction mixture is initially low in hydrazine, or lacking hydrazine altogether, the formation reaction predominates, if initially high in hydrazine and if the temperature of the reaction mixture is low, the decomposition reaction will predominate, after a period of induction has elapsed.

Reaction mixture composed initially of chloramine in liquid ammonia.- The procedure for making a rate measurement in this case was simpler than in the case in which hydrazine was added.

The cell was cleaned as described in the procedure for calibration. It was placed in the bath and the bath was set into operation.

About seventy milliliters of anhydrous ammonia was condensed from the gas phase into each of two transfer tubes (Figure 25). One of the tubes was graduated at ten milliliter intervals.

A transfer tube was first cleaned by washing with distilled water and then with acetone, after which it

Fig.25

was dried by a stream of dry nitrogen. The ammonia inlet tube (Figure 26) was firmly inserted in the mouth of the transfer tube. A fifty centimeter long section of rubber tubing was fitted on the horizontal limb of the outlet of the transfer tube. The other end of the rubber tube communicated with the back of the hood. The vertical limb of the outlet was capped by a few centimeters of rubber tubing closed with a cork stopper. A stream of gaseous ammonia was passed through the transfer tube to flush out moist air. The transfer tube was then inserted to the depth of the outlet tube in a bath composed of a slurry of dry ice in a fifty volume-percent solution of chloroform in carbon tetrachloride. Several ten milliliter rinsings of liquid ammonia were successively condensed in the tube and then drained out through the outlet tube without interrupting the flow of gas. The desired quantity of anhydrous ammonia was then collected, the ammonia inlet tube was removed and replaced with a rubber stopper. Both openings of the outlet tube were capped and the tube of ammonia was stored in a dry ice bath.

At all times during the rinsing and condensation procedures the ammonia pressure was maintained above atmospheric pressure to prevent the ingress of water vapor to the tube.

-76-

No. 6 rubber
stopper

(Actual size)

Ammonia Inlet Tube

Fig.26

The chloramine generator was set into operation to produce chloramine at the rate of approximately 60 millimoles per hour. The gas flows were adjusted so that the flow meter manometers read pressures in the order of 150 mm. of mercury, 300 mm. of methyl salicylate and 120 mm. of sulfuric acid above atmospheric pressure for the gases, ammonia, nitrogen, and chlorine, respectively. These pressures were equivalent of the flows of 2,820 millimoles per hour of ammonia, 390 millimoles per hour of nitrogen and 60 millimoles per hour of chlorine.

Chloramine was collected in the graduated transfer tube into which seventy milliliters of ammonia had been collected as described above. The stopper in the transfer tube was replaced with the chloramine inlet tube (Figure 27) and, without removing the transfer tube from the dry ice bath in which it was stored, it was connected into the by-pass circuit of the chloramine generator as shown in Figure 6. The use of the by-pass circuit permitted the chloramine generator to be set into operation for ten or fifteen minutes to attain a uniform and reproducible composition of effluent gases before condensing them in the transfer tube for a measured interval of time to condense a sample of predetermined size.

The temperature in the vicinity of the inlet tube

Fig.27

during the condensation of the chloramine and the ammonia associated with it rose from the freezing point of the solvent ammonia to the boiling point of the ammonia. To minimize reaction prior to placing the mixture in the conductivity cell, this local heat was dissipated by mixing the condensate with the larger body of cold ammonia already present. The length of the chloramine inlet tube was adjusted so that the gases were introduced well below the surface of the ammonia already in the tube, the flow of the gases thus mixing the solution. The solvent ammonia was stored usually from one to one-and-one-half hours in the dry ice bath to make certain it was near its freezing point before collecting chloramine. When the solvent was frozen in a thin shell adjacent to the cell wall, the liquid was considered to be sufficiently cold. Too much solidification reduced the volume of liquid and the resultant chloramine solution underwent more extensive reaction because it was more concentrated.

The transfer tube and chloramine inlet tube were then disconnected from the chloramine by-pass circuit as a unit. The upper portion of the chloramine inlet tube was capped with a ball joint which terminated in a small diameter glass tube inserted in a length of rubber tubing plugged with a cork stopper. The horizontal outlet of the transfer tube was capped, and without being removed from the dry ice bath, the entire unit was placed

near the thermostatic bath containing the conductivity cell.

The outlets of the transfer tube were uncapped, the upper portion of the chloramine inlet tube was removed and the lower portion of the tube used to mix the solution a few moments as it was being withdrawn from the transfer tube. A syphon tube (Figure 28) was fitted firmly in the neck of the transfer tube. The transfer tube was then removed from the ice bath and elevated so that the narrow limb of the syphon tube could be inserted into the neck of the conductivity cell as far as the middle of the expansion bulb. Dry nitrogen was introduced into the horizontal limb of the transfer tube while the vertical limb was fingered in such a way that after several progressively larger starts up the syphon tube to cool the tube the solution was forced into the conductivity cell. After all the liquid was transferred, a stream of acetone was directed on the outer surface of the transfer tube to melt some of the frozen ammonia remaining in the bottom of the tube. This ammonia was then transferred into the cell carrying most of the remaining solute with it. The time of the transfer was noted.

The other transfer tube containing ammonia only was next fitted with a syphon tube and enough ammonia

was forced out to fill the conductivity cell to a point within the volumetric lines when the solution had attained bath temperature. The time of the transfer was noted.

The solution was mixed by dry nitrogen for half a minute in the manner described under the procedure for cell calibration and a resistance reading was made. The time was noted. If the reaction was rapid, the resistance reading was made without waiting for the bath to reach a definite point in the heating cycle.

The mixing was repeated between successive readings. After ten or twelve such mixings during the first ten or fifteen minutes of the experiment the mixing was discontinued, but the readings were continued as frequently as the rate of the reaction indicated was necessary to define the curve. One mixing was made after half an hour or so to minimize any concentration gradients which might have developed. In very long experiments additional mixings were made. There was some volume decrease associated with the mixing process which resulted from the evaporation of the solvent. Because of this and other possibly unobservable changes, such as loss of chloramine by evaporation, it was thought wise to minimize the time of mixing.

The reaction was terminated at the discretion of the experimenter by converting the unreacted chloramine to

ammonium chloride through its reaction with hydrazine. The volume of the cell contents was first observed, then one half to one milliliter of pure hydrazine was introduced into the cell. The hydrazine was removed from storage in glass through a serum bottle stopper by means of a two milliliter hypodermic syringe equipped with a one inch, number 26 gauge needle. The needle was then replaced with a three inch, number 22 spinal needle, and the needle inserted for its full length in the neck of the conductivity cell. However, the needle tip was above the liquid surface. The transfer of hydrazine was immediately begun, though not rapidly effected. Delay in transfer allowed the hydrazine to freeze in the tip of the needle; rapid transfer, especially of a milliliter of hydrazine, tended to overheat the solvent locally. This heat plus the rapid evolution of nitrogen that accompanied the reaction occasionally caused the solution to boil out of the cell. After a few minutes delay to allow time for the dissipation of heat, the cell contents were well mixed and the final resistance and final volume were noted.

Information was thus obtained with which to correct this terminal value of the ammonium chloride concentration to its equivalent value had no volume change been associated with the addition of hydrazine or the evaporation of ammonia in the act of the final mixing.

Reaction mixture composed initially of chloramine and hydrazine or chloramine, hydrazine, and ammonium chloride in liquid ammonia.- The procedure for performing a rate experiment was modified in the cases where hydrazine or hydrazine plus ammonium chloride were added initially to the reaction mixture.

The transfer tube for ammonium chloride and hydrazine solutions (Figure 29) was cleaned in the same fashion as the other transfer tubes except that all rinsings were flushed out the capillary outlet tube. The capillary outlet was capped and the desired quantity of liquid ammonia was condensed in the tube. If hydrazine was to be added it was introduced from the same hypodermic syringe and spinal needle as were described above. The syringe, needle, and contents were weighed before and after the transfer of the sample. The quantity of hydrazine used was of the order of 0.10-0.20 grams, corresponding to one or two small drops from the needle tip. Evaporation from the drop surface during transfer tended to render the weight uncertain.

If ammonium chloride was to be used, it was the material, relatively free of trace metals, scraped from the inner walls of the reactor of the chloramine generator that was employed. This was weighed into the tube as described under the procedure for calibration of the

Ammonium Chloride-Hydrazine Transfer Tube

Fig.29

conductivity cell.

The mixing gas inlet tube (Figure 30) was fitted in the neck of the transfer tube and dry nitrogen was used to mix the solution. The solution was also mixed by dry nitrogen blown back through the capillary outlet of the transfer tube when the presence of undissolved ammonium chloride crystals in the bend of the capillary tube was suspected.

After the solution was mixed, the mixing tube was removed, the transfer tube was stoppered, the openings capped, and the tube stored in a dry ice bath until the solution was needed.

The solution, or part of it, was transferred to the conductivity cell containing the chloramine solution. Usually it was necessary to melt the ammonia in the capillary outlet tube before forcing all, or a measured part of the solution through the capillary into the conductivity cell. The frozen solvent ammonia inside the tube was melted by directing a stream of acetone on the surface of the transfer tube, and this ammonia served as a rinse liquid for removing most of the remaining solute from the tube to the cell. The practice of transferring only a portion of a more concentrated solution to the conductivity cell was discontinued in favor of transferring all of a more dilute solution, since the

Mixing Gas Inlet Tube for Ammonium Chloride-
Hydrazine Transfer Tube

Fig.30

presence of frozen solvent in the tube rendered the former procedure inaccurate.

The contents of the conductivity cell were diluted with ammonia to within the volumetric lines and were well mixed by a stream of dry nitrogen. The volume was noted, the resistance readings were taken, and the progress of the reaction followed as noted above.

Determination of the Stoichiometry of the Decomposition

Reaction

Need for the measurement of the stoichiometry of the decomposition reaction.- The development of the understanding of the reactions of the Raschig synthesis in water solution is outlined in the introductory section of this work.⁵² But, as was pointed out in the section dealing with the statement of the problem,⁵³ the stoichiometry indicated in equation (9) for the decomposition reaction,

$$\text{N}_2\text{H}_4 + 2\text{NH}_2\text{Cl} \longrightarrow \text{N}_2 + 2\text{NH}_4\text{Cl}, \quad (9)$$

had not been verified for the case of the reaction in liquid ammonia.

Laitinen⁵⁴ expressed doubt as to the exact

⁵² See pp. 2-6.

⁵³ See pp. 15-16.

⁵⁴ H. A. Laitinen, "Lower Oxidation States in Liquid Ammonia" (Final Report to the Office of Naval Research, Contract Nonr. 21900NR052247), p.24.

stoichiometry of the reaction of chloramine with hydrazine in liquid ammonia. He listed equation (9) and equation (12), as possible equations.

The confirmation of the stoichiometry was deemed necessary to justify methods used for computing concentrations of reactants and products in the kinetic calculations.

Summary of methods for ascertaining the stoichiometry of the decomposition reaction.- Three methods of obtaining the stoichiometry were used. They gave comparable results within the experimental errors of the determinations.

They were all based on the experimental observation that the decomposition reaction is much faster than the formation reaction described in equation (7) which follows

It was found possible, therefore, to measure the stoichiometry of the decomposition reaction practically unhindered by the formation reaction at low temperatures.

The first method was based on a comparison of the number of moles of nitrogen evolved from a mixture of hydrazine and chloramine in liquid ammonia with the number of moles of ammonium chloride formed as measured conductimetrically.

The second method was based on a comparison of the

number of moles of hydrazine consumed, as measured by introducing a weighed sample of hydrazine into a solution of excess chloramine in ammonia, with the number of moles of ammonium chloride formed, as measured conductimetrically. The stoichiometric point was marked by a conspicuous decrease in the reaction rate.

The third method was based on a comparison of the number of moles of chloramine equivalent to the moles of hydrazine consumed in those reactions which, like that of Experiment 24 (Figure 53) proceeded for several hundred minutes and then exhibited a sharp increase in reaction rate or a "break". It was considered that the hydrazine was formed in the portion of the reaction that occurred before the break, i.e., before decomposition reaction began, and, hence, the quantity of hydrazine was considered as equivalent of the ammonium chloride formed before the break. The chloramine consumed from the beginning of the break until the reaction was substantially over was considered to have reacted with the hydrazine formed before the break. The chloramine thus consumed was equivalent of the ammonium chloride formed after the break. Therefore, the post break increase in moles of ammonium chloride (change in concentration times volume) was divided by the pre-break increase in moles of ammonium chloride to obtain the ratio of chloramine to hydrazine in the decomposition reaction.

Procedure for measuring the stoichiometry of the decomposition reaction by the method of gas evolution.-

The experimental problem consisted of putting together in a vessel a relatively concentrated solution of hydrazine and a dilute solution of chloramine in such a way that the normally very rapid reaction could be retarded and the associated violent evolution of nitrogen could be controlled while the measurement of the gas volume was being made.

The apparatus consisted of a conductivity cell with the electrodes placed high on the sides of the cell. Conductivity Cell No. 4 (Figure 13) is of this design. A gas burette (Figure 31) was connected to the top of the conductivity cell by a ball joint. The gas burette and levelling bulb were filled with mercury.

Liquid ammonia was condensed in a transfer tube (Figure 25) and hydrazine was weighed into it by difference from a hypodermic syringe. The solution was mixed and forced through a syphon tube into the conductivity cell by the pressure of dry nitrogen. Details of the manipulative procedure are described in the sections on calibrating the conductivity cell and making a rate measurement. The hydrazine solution came to a depth in the conductivity cell just below the level of the lower electrode. The cell was inserted into liquid nitrogen to a height just

Gas Burette and
Leveling Bulb

Fig.31

less than the height of the lower electrode and the solution was completely frozen. Since the eutectic temperature of hydrazine-ammonia solutions is -80°C . which is just below dry ice temperatures, liquid nitrogen was the most convenient means of freezing the mixture. The placement of the electrodes prevented their exposure to the shock of liquid nitrogen temperatures.

Approximately three millimoles of chloramine were collected in forty milliliters of liquid ammonia contained in a transfer tube and thoroughly cooled in a dry ice bath.

The conductivity cell was removed from the liquid nitrogen and transferred to the thermostatic bath at -75°C . Immediately the chloramine solution was introduced into it from the transfer tube. The solution was brought up to the volumetric mark in the conductivity cell by the addition of liquid ammonia from a third transfer tube which had been stored for some time in a dry ice bath. At this point there were three layers in the cell: beginning at the bottom a frozen mixture of hydrazine and ammonia; a liquid solution of chloramine in ammonia; and, on top, liquid ammonia. Since the hydrazine solution melted very slowly in a bath at -75°C ., there was ample time for subsequent steps.

To give a reproducible and meaningful value to the final corrected volume of nitrogen evolved in the decomposition reaction, it was necessary that the upper spaces of the conductivity cell contain a fixed gas, nitrogen, saturated with ammonia vapor at the partial pressure existing above ammonia at the temperature of the bath before the gas burette was connected. It was found that this space was at first filled with ammonia vapors alone as the result of boiling a little of the ammonia solutions as they passed over the warm upper surfaces of the conductivity cell. The ammonia condensed when thermal equilibrium was achieved and a "suck back" occurred in the system. If the reverse condition prevailed, i.e., if the spaces had just been flushed free of ammonia vapor by nitrogen, to a lesser extent, there was an increase in volume as the ammonia added its vapor to the nitrogen already present. If the liquid ammonia inside the cell happened to extend higher than the cooling bath on the outside, the uncooled portion exerted a correspondingly high vapor pressure and forced ammonia out to the atmosphere through the mercury in the gas burette.

The reaction mixture was thus constituted and allowed to stand for as many as eight to twenty-four hours until the evolution of gas had terminated.

The decomposition reaction was retarded because of the time required for the melting of the hydrazine solution and for the diffusion of the hydrazine into the chloramine layer, and for the diffusion of chloramine into the hydrazine layer. When the reaction was completed, as judged by the fact that there was no further gas evolution in a period of more than two hundred minutes, the gas volume was noted, the burette was disconnected and the cell contents were mixed with a stream of dry nitrogen until the resistance reading was constant. The total volume of the liquid phase and the resistance reading were recorded.

Procedure for measuring the stoichiometry of the decomposition reaction by the use of weighed samples of hydrazine.- The various steps used in this procedure are described in detail under the procedures for calibrating the conductivity cell and making a rate measurement.⁵⁵ Weighed quantities of hydrazine, 0.01-0.02 grams (0.5-1.0 millimoles), and excess chloramine 3-4 millimoles, both in liquid ammonia solution, were introduced into the conductivity cell and diluted to the volumetric mark with liquid ammonia. The solution was mixed and resistance readings were recorded versus elapsed time.

⁵⁵ See pp. 49-51 and 73-88.

The mixing required only a few minutes, as evidenced by the steady conductivity readings obtained after a short interval. In some cases there was a temporary increase in the resistance of the solution as diluting ammonia was mixed into the more concentrated solutions in the vicinity of the electrodes.

The bath was held at -75°C . in order to minimize the formation reaction which is much more temperature dependent than the decomposition reaction.

After a period of induction, varying from a few minutes to a few hundred minutes depending upon initial concentrations of chloramine and hydrazine and probably on the presence of metal catalysts and other factors, the reaction became rapid and proceeded until the hydrazine present was consumed, or almost consumed. Since greater than stoichiometric amounts of chloramine were present, depletion of the reactants occurred first with respect to hydrazine. Thereafter, there was a marked decrease in the reaction rate and inspection of the plot of reciprocal resistance versus time showed a rather well defined decrease in the slope. The concentrations at this point were considered end-point concentrations for the decomposition reaction.

Procedure for the measurement of the stoichiometry of the decomposition reaction by comparison of pre-break and post break quantities of ammonium chloride.- The procedure was identical with the procedure for making a rate measurement using only chloramine and ammonia. Since the break was not often observed at the lower temperatures, this measurement was best made at -50 or -38°C. The break was more likely to occur at higher chloramine concentrations.

DATA AND RESULTS

Reduction of the Calibration Data of the Conductivity

Cells to an Equation in Two Parameters

As has already been pointed out⁵⁶ it was found that the logarithm of the reciprocal of the cell resistance gave a straight line graph when plotted against the logarithm of the ammonium chloride concentration. The equation was

$$\log \text{ recip.resist.} = a \log \text{ conc.} + b \quad (13)$$

where the reciprocal cell resistance was expressed in mhos and the concentration of the ammonium chloride in moles per liter of solution.

The data giving this straight line relationship can be summarized by a statement of the numerical values of the slope and the intercept, a different pair of values being used for each cell at each temperature at which it was calibrated.

Evaluation of the slope, "a", by the use of two pairs of points from the graph gives

$$\log \text{ recip.resist.} = \frac{\log (\text{recip.resist.}_2 - \log \text{ recip.resist.}_1)}{\log \text{ conc.}_2 - \log \text{ conc.}_1} \log \text{ conc.} + b \quad (14)$$

⁵⁶ See pp. 51 and 64.

Where the subscripts refer to the first and second pair of points. The expression for the slope can be written in the form

$$a = \frac{\log \left(\frac{\text{recip.resist.}_2}{\text{recip.resist.}_1} \right)}{\log \left(\frac{\text{conc.}_2}{\text{conc.}_1} \right)} \quad (15)$$

The observed relationship between concentration and reciprocal resistance may be expressed more conveniently for subsequent use as

$$\log \text{ conc.} = \frac{1}{a} \log \text{ recip.resist.} - \frac{b}{a}. \quad (16)$$

It is in this form that it is used to convert measurements of reciprocal cell resistance to the equivalent concentrations of ammonium chloride. It was considered a matter of convenience and accuracy to be able to convert conductivity data to concentration data through this equation without making reference to the calibration graphs.

Table 3 provides calculations leading to values of a , b , $\frac{1}{a}$, and $-\frac{b}{a}$. For convenience in later work it is useful to define the terms A and B which are equal to $\frac{1}{a}$ and $10^{-\frac{b}{a}}$ respectively.

Methods of Calculating Concentration in the Reaction

Mixture

It was shown in the preceeding section that the concentration of ammonium chloride in the reaction mixture

Table 3 Calculation of Slope and Intercept for
Conductivity Cell Calibration Graphs

Cell Number	Temp. °C	Conc., NH ₄ Cl moles/ liter x10 ³	Log conc., ₂	Recip. resist., ₂ mhos x10 ³	Log of recip. resist., ₂	Conc. NH ₄ Cl moles/ liter x10 ³	Conc., ₁ NH ₄ Cl moles/ liter x10 ³	Log conc., ₁	Recip. resist., ₁ mhos x10 ³
1	-34	10,000	-1.0000	438	-2.3391	40 ¹¹	40	-3.3979	8.46
2	-75	8,000	-1.0969	243	-2.6144	25 ¹⁴	25	-3.6021	3.83
3	-75	6,000	-1.2218	258	-2.5886	20 ¹⁶	20	-3.6690	3.97
4	-75	5,000	-1.3010	219	-2.6596	50 ¹⁶	50	-3.3010	7.13
4	-60	10,000	-1.0000	487	-2.3125	25 ¹⁵	25	-3.6021	5.41
4	-50	7,000	-1.1549	409	-2.3883	20 ¹³	20	-3.6990	5.22
4	-38	4,000	-1.3979	315	-2.4983	20 ¹³	20	-3.6990	6.23
5	-38	10,000	-1.0000	848	-2.0716	20 ¹⁶	20	-3.6990	16.3

Log of recip. resist., ₁	Log recip.resist., ₂ recip.resist., ₁	Log conc., ₂ conc., ₁	a = Log recip.resist., ₂ recip.resist., ₁	a log conc., ₂ - a log conc., ₂	Log recip.resist., ₂ - a log conc., ₂	1 a	b a
-4.0726	1.7335	2.3979	0.7229	-0.7229	-1.6162	1.3833	2.2357
-4.4168	1.8024	2.5052	0.7195	-0.7892	-1.8252	1.3899	2.5368
-4.4012	1.8126	2.4792	0.7317	-0.8940	-1.6946	1.3667	2.3160
-4.1469	1.4873	2.0000	0.7437	-0.9676	-1.6920	1.3446	2.2751
-4.2668	1.9543	2.6021	0.7510	-0.7510	-1.5615	1.3316	2.0792
-4.2823	1.8940	2.5441	0.7445	-0.8598	-1.5283	1.3432	2.0531
-0.7945	1.704	2.301	0.7405	-1.0351	-1.4666	1.3504	1.9806
-3.7878	1.7162	2.6990	0.6359	-0.6359	-1.4357	1.5726	2.2577

at any time can be obtained from the corresponding reciprocal cell resistance by application of equation (16), where the cell calibration constants, $\frac{1}{a}$ and $\frac{b}{a}$, are selected from the appropriate calibration data.

The value of the ammonium chloride concentration at any time during an experiment can not be used alone to obtain the concentrations of the other two related substances present, chloramine and hydrazine. It is necessary to know the final ammonium chloride concentration when all the chloramine that was initially present has been converted to ammonium chloride. This concentration, expressed in moles of ammonium chloride per liter of solution, is referred to by the symbol C_F . It represents the total of all the ammonium chloride present either from the conversion of the chloramine or from the ammonium chloride initially present.

In order to convert the chloramine to ammonium chloride as the terminal step in a rate experiment a large excess of hydrazine was added. The chloramine reacted at once and, after proper mixing, the final resistance was measured. The concentration of ammonium chloride derived from this reading was corrected for the dilution by the hydrazine added, and it was this corrected final concentration that was termed C_F .

The equation used for calculating C_F , beginning with equation (13) is derived in the following steps:

$$\log \text{ recip.resist.}_2 = a \log \text{ conc.}_2 + b \quad (17)$$

$$\log \text{ recip.resist.}_1 = a \log \text{ conc.}_1 + b \quad (18)$$

$$\log \left(\frac{\text{recip.resist.}_2}{\text{recip.resist.}_1} \right) = a \log \left(\frac{\text{conc.}_2}{\text{conc.}_1} \right) \quad (19)$$

$$\log \text{ recip.resist.}_2 = a \log \frac{\text{conc.}_2}{\text{conc.}_1} + \log \text{ recip.resist.}_1 \quad (20)$$

$$\text{conc.}_2 = \frac{n}{v_2} \quad ; \quad \text{conc.}_1 = \frac{n}{v_1} \quad (21)$$

$$\begin{aligned} \log \text{ recip.resist.}_2 = \\ a \log \left(\frac{\frac{n}{v_2}}{\frac{n}{v_1}} \right) + \log \text{ recip.resist.}_1 \end{aligned} \quad (22)$$

$$\begin{aligned} \log \text{ recip.resist.}_2 = \\ a \log \frac{v_1}{v_2} + \log \text{ recip.resist.}_1 \end{aligned} \quad (23)$$

The reciprocal resistance, thus corrected for dilution by hydrazine, is substituted in equation (16).

$$\log C_F = \frac{1}{a} \log \text{ recip.resist.}_2 - \frac{b}{a} \quad (24)$$

The subscript "1" refers to the conditions that prevail in the solution after dilution with hydrazine, and the subscript "2" refers to the conditions that would prevail if the solution occupied the volume it

occupied before excess hydrazine was added. The symbol, "v", refers to the volume of the solution, and "n" refers to the total number of moles of ammonium chloride in the solution.

A tabulation of the calculations leading to a value of C_F for each of the forty-four rate measurements is given in Table 4.

The calculation of the chloramine and hydrazine concentrations in a reaction mixture at a given time are possible if the corresponding value of the reciprocal of the cell resistance and C_F for that reaction mixture are both known, and provided several rather well justified assumptions about the course of the reaction are allowed.

The first of these assumptions is that the formation reaction, equation (7)

proceeds alone and practically uncomplicated by the decomposition reaction for a variable but definitely observable portion of the course of the reaction. As evidence in support of the assumption it can be cited that in this region the concentration order of the reaction with respect to chloramine (Figure) is $1.00 \pm .02$ and the specific reaction rate constants show no drift. (Figures and Table).

Table 4 Calculation of the Corrected Final Reciprocal Resistance and Equivalent Ammonium Chloride Concentration for the Rate Experiments R1-75 through R44-38

Calculation of the Corrected Final Reciprocal Resistance and Equivalent Ammonium Chloride Concentration for the Rate Experiments R1-75 through R44-38

Experiment number	$\frac{v_1}{v_2}$	$a \log \frac{v_1}{v_2}$	Recip. resist ₁ mhos ₁ x 10 ⁵	$\log mhos_1$	$a \log \frac{v_1}{v_2} + \log mhos_1$	Recip. resist ₂ mhos ₂ x 10 ⁵	$a \log \frac{v_1}{v_2}$	Recip. resist ₁ mhos ₁ x 10 ⁵	$\log mhos_1$	$a \log \frac{v_1}{v_2} + \log mhos_1$	Recip. resist ₂ mhos ₂ x 10 ⁵	$\frac{1}{a} \log mhos_2$	$\frac{1}{a} \log mhos_2 - \frac{b}{a}$	C _F moles/liter x 10 ³
a=0.7317						a=0.7317						$\frac{1}{a}=1.3667$ $-\frac{b}{a}=2.3160$		
R 1-75	1.0139	0.00439	81.63	-3.08815	-3.08376	82.4639	0.00439	81.63	-3.08815	-3.08376	82.46	-4.2146	-1.8986	12.630
R 2-75	1.0128	0.00404	96.15	-3.01705	-3.01301	97.0528	0.00404	96.15	-3.01705	-3.01301	97.05	-4.1179	-1.8019	15.778
R 3-75	1.0096	0.00304	99.10	-3.00393	-3.00089	99.8096	0.00304	99.10	-3.00393	-3.00089	99.80	-4.1013	-1.7853	16.394
R 4-75	1.0303	0.00948	82.30	-3.08460	-3.07512	84.15303	0.00948	82.30	-3.08460	-3.07512	84.15	-4.2028	-1.8868	12.977
R 5-75	1.0143	0.00451	113.64	-2.94447	-2.93996	114.83143	0.00451	113.64	-2.94447	-2.93996	114.83	-4.0180	-1.7020	19.861
R 6-75	1.0084	0.00266	111.11	-2.95425	-2.95159	111.80084	0.00266	111.11	-2.95425	-2.95159	111.80	-4.0339	-1.7179	19.146
R 8-75	1.0142	0.00448	59.52	-3.22534	-3.22086	60.14142	0.00448	59.52	-3.22534	-3.22086	60.14	-4.4019	-2.0859	8.205
R 9-75	1.0106	0.00335	105.30	-2.97757	-2.97422	106.12106	0.00335	105.30	-2.97757	-2.97422	106.12	-4.0649	-1.7489	17.828
R10-75	1.0098	0.00310	103.09	-2.98778	-2.98468	103.59098	0.00310	103.09	-2.98778	-2.98468	103.59	-4.0792	-1.7632	17.250
R11-75	1.0098	0.00310	99.01	-3.00432	-3.00122	99.74098	0.00310	99.01	-3.00432	-3.00122	99.72	-4.1018	-1.7858	16.376
R12-75	0.9971	0.00092	158.73	-2.80934	-2.81026	154.75971	0.00092	158.73	-2.80934	-2.81026	154.79	-3.8408	-1.5248	29.867
R13-75	1.0056	0.00177	120.48	-2.91908	-2.91731	120.93056	0.00177	120.48	-2.91908	-2.91731	120.97	-3.9871	-1.6711	21.326
R14-75	1.0084	0.00266	133.33	-2.87507	-2.87241	134.15084	0.00266	133.33	-2.87507	-2.87241	134.15	-3.9257	-1.6097	24.565
R15-75	1.0056	0.00771	114.94	-2.93953	-2.93776	115.43056	0.00771	114.94	-2.93953	-2.93776	115.41	-4.0150	-1.6990	19.999
R16-75	1.0385	0.01201	158.73	-2.80934	-2.79733	159.43385	0.01201	158.73	-2.80934	-2.79733	159.47	-3.8231	-1.5071	31.110
R17-75	1.0070	0.00222	121.95	-2.91382	-2.91160	122.57070	0.00222	121.95	-2.91382	-2.91160	122.57	-3.9793	-1.6633	21.712
R18-75	1.0070	0.00222	147.06	-2.83266	-2.83044	147.76070	0.00222	147.06	-2.83266	-2.83044	147.76	-3.8684	-1.5524	28.675
a=0.7437						a=0.7437						$\frac{1}{a}=1.3446$ $-\frac{b}{a}=2.2751$		
R19-75	1.0169	0.00541	102.04	-2.99138	-2.98597	103.25169	0.00541	102.04	-2.99138	-2.98597	103.28	-4.0149	-1.7398	18.205
R20-75	1.0056	0.00180	50.50	-3.29671	-3.29491	50.75056	0.00180	50.50	-3.29671	-3.29491	50.71	-4.4303	-2.1552	6.995
R22-75	1.0021	0.00068	120.48	-2.91908	-2.91840	120.65021	0.00068	120.48	-2.91908	-2.91840	120.69	-3.9241	-1.6490	22.439
a=0.7510						a=0.7510						$\frac{1}{a}=1.3316$ $-\frac{b}{a}=2.0792$		
R24-60	1.0069	0.00224	164.20	-2.78463	-2.78239	165.05069	0.00224	164.20	-2.78463	-2.78239	165.05	-3.7050	-1.6298	23.453
R23-60	1.0070	0.00228	176.99	-2.75205	-2.74977	177.94070	0.00228	176.99	-2.75205	-2.74977	177.92	-3.6616	-1.5824	26.158
R25-60	1.0000	0.00000	188.67	-2.72430	-2.72430	188.67000	0.00000	188.67	-2.72430	-2.72430	188.67	-3.6277	-1.5485	28.284

Table 4 Calculation of the Corrected Final Reciprocal Resistance and Equivalent Ammonium Chloride Concentration for the Rate Experiments R1-75 through R44-38 (cont.)

Experiment number	$\frac{v_1}{v_2}$	$a \log \frac{v_1}{v_2}$	Recip. resist ₁ mhos ₁ x 10 ⁵	log mhos ₁	$a \log \frac{v_1}{v_2} + \log \text{mhos}_1$	Recip. resist ₂ mhos ₂ x 10 ⁵	$a \log \frac{v_1}{v_2}$	Recip. resist ₁ mhos ₁ x 10 ⁵	log mhos ₁	$a \log \frac{v_1}{v_2} + \log \text{mhos}_1$	Recip. resist ₂ mhos ₂ x 10 ⁵	$\frac{1}{a} \log \text{mhos}_2$	$\frac{1}{a} \log \text{mhos}_2 - \frac{b}{a}$	C _F moles/liter x 10 ³
R26-60	1.0007	0.00022	195.31	-2.70927	-2.70905	195.41007	0.00022	195.31	-2.70927	-2.70905	195.41	-3.6074	-1.5282	29.635
R27-60	1.0028	0.00091	194.93	-2.71012	-2.70921	195.44028	0.00091	194.93	-2.71012	-2.70921	195.44	-3.6076	-1.5284	29.621
R28-60	1.0000	0.00000	144.51	-2.84010	-2.84010	144.51000	0.00000	144.51	-2.84010	-2.84010	144.51	-3.7819	-1.7027	19.829
		$a=0.7445$					$a=0.7445$					$\frac{1}{a}=1.3432$	$-\frac{b}{a}=2.0531$	
R29-50	1.0029	0.00094	201.21	-2.69635	-2.69541	201.64029	0.00094	201.21	-2.69635	-2.69541	201.64	-3.6205	-1.5674	27.077
R30-50	1.0007	0.00022	205.76	-2.68664	-2.68642	205.86007	0.00022	205.76	-2.68664	-2.68642	205.86	-3.6084	-1.5553	27.842
R31-50	1.0018	0.00058	182.82	-2.73797	-2.73739	183.07018	0.00058	182.82	-2.73797	-2.73739	183.07	-3.6769	-1.6238	23.779
R32-50	1.0010	0.00032	180.50	-2.74352	-2.74320	180.63010	0.00032	180.50	-2.74352	-2.74320	180.63	-3.6867	-1.6336	23.249
R33-50	1.0008	0.00026	170.94	-2.76716	-2.76690	171.04008	0.00026	170.94	-2.76716	-2.76690	171.04	-3.7165	-1.6634	21.707
R34-50	1.0028	0.00090	216.45	-2.66464	-2.66374	216.90028	0.00090	216.45	-2.66464	-2.66374	216.90	-3.5779	-1.5248	29.867
R35-50	0.9986	0.00045	249.38	-2.60314	-2.60359	249.12986	0.00045	249.38	-2.60314	-2.60359	249.12	-3.4971	-1.4440	35.975
		$a=0.7405$					$a=0.7405$					$\frac{1}{a}=1.3504$	$-\frac{b}{a}=1.9806$	
R36-38	1.0000	0.00000	187.26	-2.72755	-2.72755	187.26000	0.00000	187.26	-2.72755	-2.72755	187.26	-3.6833	-1.7027	19.829
R37-38	1.0000	0.00000	213.68	-2.67024	-2.67024	213.68000	0.00000	213.68	-2.67024	-2.67024	213.68	-3.6059	-1.6253	23.697
R38-38	1.0035	0.00112	180.18	-2.74430	-2.74318	180.64035	0.00112	180.18	-2.74430	-2.74318	180.64	-3.1044	-1.7238	18.889
R39-38	1.0014	0.00045	185.18	-2.73241	-2.73196	185.37014	0.00045	185.18	-2.73241	-2.73196	185.37	-3.6892	-1.7086	19.561
R40-38	1.0000	0.00000	254.45	-2.59440	-2.59440	254.45000	0.00000	254.45	-2.59440	-2.59440	254.45	-3.5035	-1.5229	29.998
		$a=0.6359$					$a=0.6359$					$\frac{1}{a}=1.5726$	$-\frac{b}{a}=2.2577$	
R41-38	1.0068	0.00187	307.69	-2.51188	-2.51001	309.02068	0.00187	307.69	-2.51188	-2.51001	309.02	-3.9472	-1.6895	20.441
R42-38	1.0068	0.00187	389.10	-2.40994	-2.40807	390.28068	0.00187	389.10	-2.40994	-2.40807	390.28	-3.7869	-1.5292	29.567
R43-38	1.0000	0.00000	500.00	-2.30103	-2.30103	500.00000	0.00000	500.00	-2.30103	-2.30103	500.00	-3.6186	-1.3609	43.561
R44-38	1.0000	0.00000	454.54	-2.34243	-2.34243	454.54000	0.00000	454.54	-2.34243	-2.34243	454.54	-3.6837	-1.4260	37.497

Calculation of the Corrected Final Reciprocal Resistance and Equivalent Ammonium Chloride Concentration for the Rate Experiments R1-75 through R44-38 (cont.)

Within this region the stoichiometric relations of equation (7) are obeyed. The ammonium chloride formed is equal to the chloramine consumed or to twice the hydrazine formed. The actual concentration of ammonium chloride, as differentiated from a change in concentration, can be found at a given time from the corresponding reciprocal cell resistance through equation (16). The concentration of the chloramine remaining unreacted at any given time can be found from the difference in C_F and the corresponding concentration of ammonium chloride, since C_F differs from the ammonium chloride concentration by the quantity of chloramine available to be converted to ammonium chloride.

The hydrazine concentration is equal to half the ammonium chloride concentration at any time within this region if there is no other source of ammonium chloride or hydrazine than that produced in the reaction of chloramine with ammonia. If there is an external source of either, the calculations can be appropriately adjusted to account for it.

The initiation of the decomposition reaction is evidenced by a sharp rise in the rate of formation of ammonium chloride. An abrupt "break" occurs in the rate measurement graph. This is demonstrated in the case of Experiment 24 (Figure 53). When all the

hydrazine present has been consumed by chloramine the reaction rate decreases conspicuously. For a rate measurement to be adaptable to the calculations now to be described, it is necessary that there be chloramine in excess of the hydrazine present at the time the decomposition reaction begins. When the decomposition reaction becomes dominant, it is so much faster than the formation reaction that the contribution from the formation reaction at low temperatures, at least, is negligible, and at higher temperatures it may be corrected for. It was found that this correction did not exceed five percent in most cases.

It was found that the decomposition reaction follows the stoichiometry of equation (9).

The stoichiometry was confirmed by three different methods of measurement.⁵⁷

In the region beyond the break the ammonium chloride and chloramine are calculated as described for the region before the break. After the break the hydrazine is thought to begin to diminish rather than increase with increasing ammonium chloride concentration.

⁵⁷

See pp. 88-97 and 108-115.

The relationship follows the stoichiometry of the decomposition reaction. The concentration of the hydrazine present just at the beginning of the break is taken as equal to half the ammonium chloride concentration increase in the region from the beginning of the break until the end of the rapid reaction. This is a measure of all the hydrazine present regardless of its source. The concentration of the hydrazine at any point within the region of the break is taken as equal to half the increase in ammonium chloride concentration from that point to the point marking the end of the rapid reaction. In this work calculations of hydrazine concentration were usually made in regions after the break.

Results of the Stoichiometry Measurement

The stoichiometry of the decomposition reaction was verified in three different types of measurements as described in the section on experimental procedures.⁵⁸ The results of these measurements are considered here in the order in which the methods were described: the method of gas evolution, the method of weighed samples of hydrazine, and the method of comparison of pre-break and post break quantities of ammonium chloride.

⁵⁸ See pp. 89-97.

Results by the method of gas evolution.- Experiment numbers of this series of measurements conducted solely for the purpose of determining stoichiometry are identified by the series letter, "S", for "stoichiometry". They carry a superscript indicating the temperature of the measurement. Experiment three conducted at -75°C . is numbered, accordingly, "S3⁻⁷⁵"

The ratio of the number of molecular weights of ammonium chloride formed to moles of nitrogen evolved in the decomposition were compared. The nitrogen evolved was measured in a gas burette. The number of molecular weights of ammonium chloride formed were obtained from the reciprocal cell resistance by use of equation (16). A correction was applied for the ammonium chloride contributed by the formation reaction which was proceeding concurrently with the retarded decomposition reaction. The formation reaction made a larger contribution to the ammonium chloride concentration in the stoichiometry measurement than it ordinarily would have done because the decomposition reaction had been slowed down. The magnitude of the correction was determined by duplicate experiments, S10⁻⁷⁵ and S13⁻⁷⁵, which were performed exactly as the others in the series except that the addition of hydrazine was omitted. The value of the correction in

molecular weights of ammonium chloride was obtained by multiplying the volume of the solution times the concentration of ammonium chloride formed in the blank experiments, 0.7×10^{-3} moles per liter. The correction was somewhat too large because the concentration of chloramine in the regular experiment was reduced by reacting with hydrazine, whereas it remained almost unchanged during the entire course of the blank experiments.

Experiment S14⁻⁷⁵ was performed to determine whether the conductance of ammonium chloride solutions in ammonia is altered by the presence of excess hydrazine. It was found that addition of hydrazine had no appreciable effect other than that attributable to dilution of the solution by the volume of the hydrazine added.

A summary of the data is provided in Table 5. The mean value of the ratio of ammonium chloride to nitrogen in the reaction products was found to be 1.92. The standard deviation of the mean was 0.0723. The mean value of the ratio is within four percent of the value 2.00 predicted by equation (9)

Table 5 Calculation of Ratios of Ammonium Chloride to Nitrogen in the Reaction Products of the Decomposition Reaction by the Method of Gas Evolution

Expt. number	Nitrogen evolved moles $\times 10^5$	NH ₄ Cl* formed moles $\times 10^5$	Ratio of NH ₄ Cl to nitrogen
S3-75	64.3	114.5	1.81
S6-75	95.6	149.0	1.56
S7-75	60.7	119.8	1.97
S8-75	69.1	114.3	1.66
S9-75	62.7	131.3	2.09
S11-75	77.5	146.0	1.88
S15-75	88.5	182.0	2.06
S16-75	50.5	102.0	2.03
S18-75	59.2	132.7	2.24
Mean value of ratio			1.92
Stand. dev. of the mean			0.0723

S10-75 Blank experiment, no hydrazine added,
 0.7×10^{-3} moles/liter NH₄Cl formed by the formation
 reaction.

S13-75 Blank experiment, no hydrazine added,
 0.6×10^{-3} moles/liter NH₄Cl formed by the formation
 reaction.

S14-75 showed no change in conductivity of solu-
 tion of ammonium chloride in liquid ammonia when excess
 N₂H₄ was added other than that attributed to dilution.

*Corrected for 0.7×10^{-3} moles/liter of NH₄Cl formed
 by the formation reaction.

The data exclude as a possibility the stoichiometric relation expressed in equation (12)

which shows a ratio of 1.00 for these quantities.

Results by the method of weighed samples of hydrazine.- The data used in this series of calculations were taken during a study of the rate of the decomposition reaction. The experiment numbers bear the identifying series letter, "R", for "rate". They carry a superscript indicating the temperature of the measurement. Experiment nine conducted at -75°C . is numbered, accordingly, "R9-75".

The calculation of the ratios of the number of molecular weights of ammonium chloride formed to hydrazine consumed at -75°C . is outlined in Table 6. It follows the method of calculating concentrations in the reaction mixture in the region beyond the break described on pages 103-107. As was noted there, the method is only applicable to cases in which the reaction mixture at the beginning of the break has an excess of chloramine. Several mixtures were composed in which chloramine was deficient. This is the case of experiments R5-75, R6-75, R8-75, and R20-75.

Table 6 Calculation of the Ratios of Ammonium Chloride Formed to Hydrazine Consumed in the Decomposition Reaction by the use of Weighed Samples of Hydrazine

Expt. Number	Corrected final conc. of NH_4Cl C_F moles/liter $\times 10^3$	Recip. resist. at end of induction period mhos $\times 10^5$	Conc. of NH_4Cl at end of induction period C_i moles/liter $\times 10^3$	Recip. resist. at end of rapid reaction mhos $\times 10^5$	Conc. of NH_4Cl at end of rapid reaction C_P moles/liter $\times 10^3$	cip. resist. end of rapid action mhos $\times 10^5$	Conc. of NH_4Cl at end of rapid reaction C_P moles/liter $\times 10^3$	Increase in conc. of NH_4Cl $C_P - C_i$ moles/liter $\times 10^3$	Vol. of solution before diluting with N_2H_4 ml.
R9-75	17.83	3.4	0.16	96.5	15.20	96.5	15.20	15.04	71.0
R10-75	17.25	4.3	0.22	54.8	7.20	54.8	7.20	6.98	71.3
R11-75	16.38	4.7	0.25	83.3	12.40	83.3	12.40	12.15	71.5
R12-75	29.87	7.9	0.51	104.5	17.60	104.5	17.60	17.09	72.5
R13-75	21.33	6.4	0.38	57.3	7.60	57.3	7.60	7.22	71.0
R14-75	24.56	22.1	2.07	73.0	10.50	73.0	10.50	8.43	71.4
R15-75	20.00	16.6	1.38	66.7	9.45	66.7	9.45	8.07	71.5
R16-75	31.10	29.3	3.04	75.9	11.30	75.9	11.30	8.26	74.4
R17-75	21.71	27.0	2.73	73.0	10.50	73.0	10.50	7.77	71.3
R18-75	28.68	38.3	4.40	80.7	12.30	80.7	12.30	7.90	71.1
R19-75	18.21	7.8	0.56	66.8	10.20	66.8	10.20	9.64	59.0
R22-75	22.44	9.0	0.68	58.8	8.50	58.8	8.50	7.82	72.1

Moles of NH_4Cl formed $\times 10^5$

Moles of N_2H_4 added

Ratio $\frac{\text{NH}_4\text{Cl}}{\text{N}_2\text{H}_4}$

106.8	63.9	1.67
49.8	33.3	1.50
86.9	51.4	1.69
123.9	68.8	1.80
51.3	34.0	1.51
60.2	35.8	1.68
57.7	37.7	1.53
61.4	32.4	1.90
55.4	33.0	1.68
56.2	32.1	1.75
56.9	32.4	1.76
56.4	31.8	1.77

Mean value of ratio- 1.687

Stand. dev. of mean- 0.0354

The mean value of the ratio of molecular weights of ammonium chloride formed to hydrazine consumed is 1.69. The standard deviation of the mean is 0.0354. The mean value of the ratio is 17.5 percent below the value, 2.00, predicted by equation (9). This result is sufficiently close to differentiate between equation (9) and (12) if it can be assumed that one or the other occurs alone, but not if both occur concurrently. Evaporation of liquid hydrazine as it is dropped from the tip of the hypodermic needle into the solvent during the preparation of the solution might well account for the low observed value of the ratio.

Results by the method of comparison of pre-break and post break quantities of ammonium chloride.- The data used in this series of calculations were taken during a study of the rate of the formation reaction at several temperatures.

On pages 90 and 103-107 there appears a description of the method of obtaining the ratio of the number of molecular weights of hydrazine produced in the formation reaction before the break to the ammonium chloride produced in the decomposition reaction that follows the break and in which the hydrazine, formed before the break, is consumed.

The results are given in Table 7. The mean value of the ratio is 1.95 after the results of experiment R36-38 are rejected. The standard deviation of the mean is 0.125. Correction was not made for the hydrazine contributed by the formation reaction after the onset of the break. The correction is larger at higher temperatures. At $-38^{\circ}\text{C}.$, the highest temperature employed, it is in the order of five percent.

The mean value of the ratio is 2.5 percent below the value, 2.00, predicted by equation (9). This result gives further support to the assumption that equation (9) represents the stoichiometry of the decomposition reaction.

Reaction Rate Measurement Data

The principal portion of the work described in this dissertation centers about the measurement of the reaction rates of the formation and decomposition reactions which follow equations (7) and (9), respectively.

The statement of the problem appears on pages 13-16 and the procedures for the measurement are given on pages 64-84. The experimental data are reported in Tables 8 through 49 and are represented graphically in

Table 7 Calculation of the Ratios of Ammonium Chloride Formed to Hydrazine Consumed in the Decomposition Reaction by the Comparison of Pre-break and Post Break Quantities of Ammonium Chloride

Expt. number	Change in conc. of NH ₄ Cl from break to end of rapid reaction B mhos _c ^A -B mhos _b ^A moles/liter x10 ³	Change in conc. of NH ₄ Cl from time zero to break B mhos _b ^A -B mhos _i ^A moles/liter x10 ³	Ratio NH ₄ Cl Post break NH ₄ Cl Pre- break
R24-60	4.846	2.486	1.95
R30-50	7.495	3.307	2.27
R31-50	11.94	6.527	1.83
R32-50	11.46	6.123	1.87
R34-50	5.417	2.674	2.02
R35-50	21.60	12.38	1.74
R36-38	10.60	2.766	3.83*
R37-38	15.44	5.751	2.68
R38-38	10.98	6.430	1.71
R39-38	10.21	8.387	1.22
R40-38	19.39	8.542	2.27
Mean value of ratio			1.95
Stand. dev. of the mean			0.125
*Rejected before taking the mean			

Figures 32 through 75.

The rate experiment numbers bear an identifying series letter, "R", for "rate" and carry a superscript indicating the temperature of the measurement. Experiment nine conducted at -75°C . is numbered, accordingly, "R9⁻⁷⁵".

The experiments performed can be classified into several types depending on their purposes and the compositions of the reaction mixtures.

Experiments R1⁻⁷⁵ through R4⁻⁷⁵ were carried out using a reaction mixture composed initially of chloramine in liquid ammonia at -75°C . and were devised for the study of the formation reaction only.

Experiments R5⁻⁷⁵ through R22⁻⁷⁵ were carried out using a reaction mixture composed initially of chloramine and hydrazine in liquid ammonia at -75°C . and were devised for the study of the decomposition reaction. They exhibit an induction period before the decomposition reaction begins. Ammonium chloride taken from the reactor tube of the chloramine generator was added to the reaction mixtures of experiments R14⁻⁷⁵ through R18⁻⁷⁵.

Experiments R23⁻⁶⁰ through R44⁻³⁸ were carried out using a reaction mixture composed initially of chloramine in liquid ammonia. Within this group of experiments temperatures employed were -60 , -50 , or -38°C ., as

indicated by the superscript on the experiment number.

These experiments were devised for the study of the formation reaction at several temperatures. However, in a progressively larger fraction of the experiments, as the temperature was elevated, the decomposition reaction also began to occur after the mixture had been standing from 400 minutes in the case of experiment R24⁻⁶⁰ to 50 minutes in the case of experiment R36⁻³⁸. In fact, in all the experiments conducted at -38°C. the decomposition reaction was observed to occur after an appropriate interval of time had elapsed. The formation reaction only was observed to occur in experiments R23⁻⁶⁰, R25⁻⁶⁰ through R28⁻⁶⁰, R29⁻⁵⁰, and R33⁻⁵⁰. The formation reaction was observed to occur alone at first, followed by a combination of the formation and decomposition reactions in the case of experiments R24⁻⁶⁰, R30⁻⁵⁰, R31⁻⁵⁰, R32⁻⁵⁰, R34⁻⁵⁰, R35⁻⁵⁰, and R36⁻³⁸ through R44⁻³⁸.

Experiments R41⁻³⁸ through R44⁻³⁸ were conducted in Conductivity Cell No. 5 (Figure 76) which was equipped with mercury free electrodes. The purpose of these experiments was to test whether mercury from the electrodes was responsible for the decomposition reaction beginning to occur. The results indicate it was not since the decomposition reaction occurred in substantially the same manner as in the cell containing mercury filled electrodes.

Table 8 Experiment Number R 1-75

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	Nov. 1, 1954
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	15 min.
Time spent in collecting chloramine	3.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.83
Volume of chloramine solution transferred to conductivity cell	50 ml.
Time of transferring chloramine solution to conductivity cell	4:22
Time of diluting near the volumetric line with liquid ammonia	4:30
Volume of cell contents at the end of the rate measurement	71.79 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	1.0 ml.
Volume of cell contents after adding hydrazine and mixing	72.79 ml.
Final conductivity reading in reciprocal ohms x 10^5 after adding hydrazine and mixing	81.63

Table 8 Experiment Number R1-75

Elapsed time		Dial	Factor	Ohms	Recip. Resist.:	
in hours	in minutes				Mhos x 10 ⁵	Log mhos
0:15	15.0	1,500	10	15,000	6.67	-4.17587
0:25	25.0	1,500	10	15,000	6.67	-4.17587
1:13	73.0	1,450	10	14,500	6.90	-4.16115
4:10	250.0	1,280	10	12,800	7.81	-4.10735
4:33	273.0	1,265	10	12,650	7.90	-4.10237
4:45	285.0	1,255	10	12,550	7.97	-4.09854
5:15	315.0	1,235	10	12,350	8.10	-4.09151
5:53	353.0	1,205	10	12,050	8.30	-4.08092
6:45	405.0	1,180	10	11,800	8.47	-4.07212
7:28	448.0	1,150	10	11,500	8.70	-4.06048
7:30	450.0	1,150	10	11,500	8.70	-4.06048
8:30	510.0	1,110	10	11,100	9.01	-4.04528
9:25	565.0	1,100	10	11,000	9.01	-4.04528
10:10	610.0	1,075	10	10,750	9.30	-4.03152
10:53	653.0	1,050	10	10,500	9.52	-4.02136
11:50	710.0	1,030	10	10,300	9.71	-4.01278
13:10	790.0	1,000	10	10,000	10.00	-4.00000
14:10	850.0	965	10	9,650	10.36	-3.98464
14.40	880.0	960	10	9,600	10.36	-3.98464
Add 1.0 ml. N ₂ H ₄						
		123	10	1,230	81.30	-3.08991
		122	10	1,220	81.97	-3.08635
		1,225	1	1,225	81.63	-3.08815

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER RI-75

Fig. 32

Table 9 Experiment Number R 2⁻⁷⁵

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of measurement	Nov. 10, 1954
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	12 min.
Time spent in collecting chloramine	3.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.85
Volume of chloramine solution transferred to conductivity cell	50 ml.
Time of transferring chloramine solution to conductivity cell	1:32
Time of diluting near the volumetric line with liquid ammonia	1:35
Volume of cell contents at the end of the rate measurement	70.59 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.9 ml.
Volume of cell contents after adding hydrazine and mixing	71.49 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	96.15
Zero time taken from first reading at 1:45	

Table 9 Experiment Number R2⁻⁷⁵

Time elapsed		Dial	Factor	Ohms	Recip. Resist.:	
in hours	in minutes				Mhos x 10 ⁵	Log mhos x 10 ⁵
0:00	0.0	1,700	10	17,000	5.88	-4.2306
0:08	8.0	1,730	10	17,300	5.78	-4.2381
0:15	15.0	1,720	10	17,200	5.81	-3.2351
0:40	40.0	1,690	10	16,900	5.92	-4.2277
1:08	68.0	1,625	10	16,250	6.15	-4.2104
1:32	92.0	1,590	10	15,900	6.29	-4.2020
1:33	93.0	1,600	10	16,000	6.25	-4.2041
2:15	135.0	1,530	10	15,300	6.54	-4.1851
2:20	140.0	1,530	10	15,300	6.54	-4.1851
2:58	178.0	1,475	10	14,750	6.78	-4.1688
4:25	265.0	1,380	10	13,800	7.25	-4.1397
7:28	458.0	1,220	10	12,200	8.20	-4.0862
8:20	500.0	1,170	10	11,700	8.55	-4.0680
9:30	570.0	1,120	10	11,200	8.93	-4.0492
10:38	638.0	1,080	10	10,800	9.26	-4.0329
11:28	688.0	1,050	10	10,500	9.52	-4.0214
12:15	735.0	1,020	10	10,200	9.80	-4.0079
13:15	795.0	1,000	10	10,000	10.00	-4.0000
Add 0.9 ml. N ₂ H ₄						
		104	10	1,040	96.15	-3.0168

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R2-75

Fig. 33

Table 10 Experiment Number R 3⁻⁷⁵

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	Nov. 15, 1954
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	12 min.
Time spent in collecting chloramine	3.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.83
Volume of chloramine solution transferred to conductivity cell	50 ml.
Time of transferring chloramine solution to conductivity cell	1:27
Time of diluting near the volumetric line with liquid ammonia	1:35
Volume of cell contents at the end of the rate measurement	73.16 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.7 ml.
Volume of cell contents after adding hydrazine and mixing	73.86 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	99.10
Zero time taken from first reading at 1:45	

Table 10 Experiment Number R3⁻⁷⁵

Elapsed time		Dial	Factor	Ohms	Recip. Resist.:	
in hours	in minutes				Mhos x 10 ⁵	Log mhos x 10 ⁵
0:00	0.0	1,730	10	17,300	5.78	-4.2381
0:15	15.0	1,690	10	16,900	5.92	-4.2277
0:37	37.0	1,630	10	16,300	6.13	-4.2118
1:22	82.0	1,580	10	15,800	6.33	-4.1986
1:43	103.0	1,550	10	15,500	6.45	-4.1898
2:27	147.0	1,470	10	14,700	6.80	-4.1669
2:59	179.0	1,440	10	14,400	6.94	-4.1586
3:47	287.0	1,380	10	13,800	7.25	-4.1397
6:25	385.0	1,230	10	12,300	8.13	-4.0899
7:05	425.0	1,178	10	11,780	8.49	-4.0716
8:52	532.0	1,115	10	11,150	8.97	-4.0472
9:35	570.0	1,090	10	10,900	9.17	-4.0372
10:51	651.0	1,055	10	10,550	9.48	-3.0232
13:03	783.0	980	10	9,800	10.20	-3.9910
13:10	790.0	970	10	9,700	10.31	-3.9863
14:00	840.0	950	10	9,500	10.53	-3.9776
14:14	854.0	950	10	9,500	10.53	-3.9776

Add 0.7 ml. N₂H₄

1,015	1	1,015	98.52
1,010	1	1,010	99.01
1,020	1	1,020	98.04
1,015	1	1,015	98.52
1,010	1	1,010	99.01

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R3-75
Fig.34

Table 11 Experiment R 4-75

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	Nov. 18, 1954
Conductivity cell number	3
Exact bath temperature	-74.3 ⁰ C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	11 min.
Time spent in collecting chloramine	3.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.83
Volume of chloramine solution transferred to conductivity cell	50 ml.
Time of transferring chloramine solution to conductivity cell	2:33
Time of diluting near the volumetric line with liquid ammonia	2:45
Volume of cell contents at the end of the rate measurement	71.66 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.9 ml.
Volume of cell contents after adding hydrazine and mixing	73.83 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	82.30
Zero time taken from first reading at 2:50	

Table 11 Experiment Number R4-75

Elapsed time		Dial	Factor	Ohms	Recip. Resist.:	
in hours	in minutes				Mhos x 10 ⁵	Log mhos x 10 ⁵
0:00	0	2,100	10	21,000	4.76	-4.3215
0:12	12	2,060	10	20,600	4.85	-4.3125
0:36	36	1,980	10	19,800	5.05	-4.2967
1:18	78	1,930	10	19,300	5.18	-4.2857
1:50	110	1,880	10	18,800	5.32	-4.2741
2:30	150	1,820	10	18,200	5.49	-4.2604
5:07	307	1,600	10	16,000	6.25	-4.2041
6:03	363	1,525	10	15,250	6.56	-4.1824
6:33	393	1,485	10	14,850	6.73	-4.1712
7:24	444	1,435	10	14,350	6.97	-4.1561
8:21	501	1,380	10	13,800	7.25	-4.1397
9:30	570	1,325	10	13,250	7.55	-4.1226
10:35	635	1,260	10	12,600	7.94	-4.1007
11:34	694	1,225	10	12,250	8.16	-4.0878
12:51	771	1,180	10	11,800	8.47	-4.0721
15:16	916	1,090	10	10,900	9.17	-4.0372
16:36	996	1,060	10	10,600	9.43	-4.0255
17:53	1,073	1,020	10	10,200	9.80	-4.0079
19:02	1,142	990	10	9,900	10.10	-3.9953
20:20	1,220	965	10	9,650	10.36	-3.9842
21:18	1,278	938	10	9,380	10.66	-3.9718
22:33	1,353	905	10	9,050	11.05	-3.9566
23:36	1,416	895	10	8,950	11.17	-3.9516
24:37	1,477	875	10	8,750	11.43	-3.9423
25:31	1,531	855	10	8,550	11.70	-3.9322
28:46	1,726	805	10	8,050	12.42	-3.9059
30:12	1,812	795	10	7,950	12.58	-3.9003
31:23	1,883	770	10	7,700	12.99	-3.8867
33:11	1,991	745	10	7,450	13.42	-3.8719
35:16	2,116	730	10	7,300	13.70	-3.8633

Table 11 Experiment Number R4-75 (cont.)

Elapsed time		Dial	Factor	Ohms	Recip. Resist.: mhos x 10 ⁵	Log mhos
in hours	in minutes					
37:39	2,220	690	10	6,900	14.49	-3.8389
39:41	2,340	675	10	6,750	14.81	-3.8292
41:55	2,515	645	10	6,450	15.50	-3.8097
44:05	2,645	635	10	6,350	15.75	-3.8036
45:25	2,725	618	10	6,180	16.18	-3.7913
47:18	2,836	610	10	6,100	16.39	-3.7854
49:04	2,945	593	10	5,930	16.86	-3.7731
52:25	3,145	567	10	5,670	17.64	-3.7538
55:26	3,326	545	10	5,450	18.35	-3.7366
57:52	3,472	540	10	5,400	18.52	-3.7321
60:30	3,630	523	10	5,230	19.12	-3.7185
62:06	3,726	510	10	5,100	19.61	-3.7073
64:39	3,879	500	10	5,000	20.00	-3.6990
66:29	3,989	490	10	4,900	20.41	-3.6899
70:22	4,222	478	10	4,780	20.92	-3.6792
71:40	4,300	472	10	4,720	21.19	-3.6733
73:09	4,389	467	10	4,670	21.41	-3.6692
77:09	4,629	453	10	4,530	22.08	-3.6568
80:16	4,816	440	10	4,400	22.73	-3.6434
81:58	4,918	432	10	4,320	23.15	-3.6355
84:31	5,071	430	10	4,300	23.26	-3.6338
86:58	5,218	422	10	4,220	23.70	-3.6249
89:44	5,384	417	10	4,170	23.98	-3.6198
91:32	5,492	410	10	4,100	24.39	-3.6130
93:57	5,637	403	10	4,030	24.81	-3.6056
96:37	5,797	394	10	3,940	25.38	-3.5957
100:54	6,054	387	10	3,870	25.84	-3.5879
104:00	6,240	374	10	3,740	26.74	-3.5732
106:30	6,390	370	10	3,700	27.03	-3.5683

Table 11 Experiment Number R4⁻⁷⁵ (cont.)

Elapsed time		Dial	Factor	Ohms	Recip. Resist.: mhos x 10 ⁵	Log mhos x 10 ⁵
in hours	in minutes					
108:49	6,5299	363	10	3,630	27.55	-3.5599
110:47	6,647	361	10	3,610	27.70	-3.5575
113:29	6,809	355	10	3,550	28.17	-3.5501
116:37	6,997	352	10	3,520	28.41	-3.5467
Add 0.9 ml. N ₂ H ₄		1,215	1	1,215	82.30	-3.0845

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R4-75

Fig.35

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R4-75

Fig. 36

Table 12 Experiment Number R 5-75

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which a weighed quantity of hydrazine was added.

Date of the measurement	March 12, 1955
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0281
Difference in height of the two limbs of the chlorine manometer expressed in mm. of sulfuric acid	120 mm.
Time spent in wasting chloramine	15 min.
Time spent in collecting chloramine	4 min.
Fraction of chloramine solution transferred to conductivity cell	0.70
Volume of chloramine solution transferred to conductivity cell	35 ml.
Time of transferring chloramine solution to conductivity cell	3:47
Time of transferring hydrazine solution to conductivity cell	3:52
Time of diluting near the volumetric line with liquid ammonia	3:56
Volume of cell contents at the end of the rate measurement	70.09 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	1.0 ml.
Volume of cell contents after adding hydrazine and mixing	71.09 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	113.64

Table 12 Experiment Number R5-75

Elapsed time in min.	Dial	Factor	Ohms	Mhos x 10 ⁵
1.5	1,570	10	15,700	6.37
2.0	1,620	10	16,200	6.17
4.0	1,650	10	16,500	6.06
6.0	1,670	10	16,700	5.99
9.0	1,630	10	16,300	6.13
19.0	1,580	10	15,800	6.33
23.0	518	10	5,180	19.30
24.0	438	10	4,380	22.83
25.0	338	10	3,380	29.58
26.3	232	10	2,320	43.10
27.4	182	10	1,820	54.94
28.3	150	10	1,500	66.67
29.6	122	10	1,220	81.97
31.0	105	10	1,050	95.24
33.0	98	10	980	102.04
34.5	90	10	900	111.11
37.0	92	10	920	108.70
42.0	92	10	920	108.70
52.0	88	10	880	113.64
Add 1.0 ml. N ₂ H ₄				
	88	10	880	113.64

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R5-75

Fig.37

Table 13 Experiment Number R 6-75

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which a weighed quantity of hydrazine was added.

Date of the measurement	June 9, 1955
Conductivity cell number	3
Exact bath temperature	74.3°C.
Weight in grams of added hydrazine	0.0119 g.
Difference in height of the two limbs of the chlorine manometer expressed in mm. of sulfuric acid	120 mm.
Time spent in wasting chloramine	15 min.
Time spent in collecting chloramine	4 min.
Fraction of chloramine solution transferred to conductivity cell	0.75
Volume of chloramine solution transferred to conductivity cell	45 ml.
Time of transferring chloramine solution to conductivity cell	6:00
Time of transferring hydrazine solution to conductivity cell	6:07
Time of diluting near the volumetric line with liquid ammonia	6:10
Volume of cell contents at the end of the rate measurement	71.09 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.6 ml.
Volume of cell contents after adding hydrazine and mixing	71.69 ml.
Final conductivity reading in reciprocal ohms $\times 10^2$ after adding hydrazine and mixing	111.11
0.0249 g. of hydrazine was added at the 70th minute of elapsed time.	

Table 13 Experiment Number R6-75

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
3.0	660	10	6,600	15.15
7.0	680	10	6,800	14.70
9.0	675	10	6,750	14.81
16.0	660	10	6,600	15.15
26.0	660	10	6,600	15.15
41.0	655	10	6,550	15.27
54.0	655	10	6,550	15.27
70.0	653	10	6,530	15.31
92.0	370	10	3,700	27.03
96.0	315	10	3,150	31.75
98.0	295	10	2,950	33.90
103.0	255	10	2,550	39.22
105.0	240	10	2,400	41.67
107.0	225	10	2,250	44.44
111.0	203	10	2,030	49.26
116.0	182	10	1,820	54.94
130.0	143	10	1,430	69.93
146.0	122	10	1,220	81.97
160.0	110	10	1,100	90.91
185.0	100	10	1,000	100.00
204.0	98	10	980	102.04
Add 0.6 ml. N ₂ H ₄				
	90	10	900	111.11

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT
NUMBER R6-75

Fig. 38

Table 14 Experiment Number R 8-75

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which a weighed quantity of hydrazine was added.

Date of the measurement	June 16, 1955
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0120 g.
Difference in height of the two limbs of the chlorine manometer expressed in mm. of sulfuric acid	120 mm.
Time spent in wasting chloramine	15 min.
Time spent in collecting chloramine	4 min.
Fraction of chloramine solution transferred to conductivity cell	0.75
Volume of chloramine solution transferred to conductivity cell	45 ml.
Time of transferring chloramine solution to conductivity cell	4:47
Time of transferring hydrazine solution to conductivity cell	4:55
Time of diluting near the volumetric line with liquid ammonia	5:00
Volume of cell contents at the end of the rate measurement	70.59 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	1.0 ml.
Volume of cell contents after adding hydrazine and mixing	71.59 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	59.57
Elapsed time measured from 5:15 as bath was off temperature until then.	

Table 14. Experiment Number R8-75

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
0.0	310	100	31,000	3.22
20.0	300	100	30,000	3.33
35.0	295	100	29,500	3.39
102.0	278	100	27,800	3.60
140.0	265	100	26,500	3.77
169.0	250	100	25,000	4.00
187.0	241	100	24,100	4.14
233.0	237	100	23,700	4.22
260.0	210	100	21,000	4.76
263.0	200	100	20,000	5.00
273.0	163	100	16,300	6.13
279.0	118	100	11,800	8.47
287.0	850	10	8,500	11.76
288.0	810	10	8,100	12.34
291.0	720	10	7,200	13.89
294.0	650	10	6,500	15.38
297.0	580	10	5,800	17.24
303.0	470	10	4,700	21.28
306.0	428	10	4,280	23.36
311.0	378	10	3,780	26.46
320.0	326	10	3,260	30.67
330.0	288	10	2,880	34.72
341.0	261	10	2,610	38.31
353.0	241	10	2,410	41.49
371.0	225	10	2,250	44.44
393.0	210	10	2,100	47.62
429.0	198	10	1,980	50.50
510.0	179	10	1,790	55.86
Add 1.0 ml. N ₂ H ₄				
	168	10	1,680	59.52
	167	10	1,670	59.88

Fig.39

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R8-75

Table 15 Experiment Number R 9-75

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which a weighed quantity of hydrazine was added.

Date of the measurement	June 23, 1955
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0205 g.
Difference in height of the two limbs of the chlorine manometer expressed in mm. of sulfuric acid	120 mm.
Time spent in wasting chloramine	15 min.
Time spent in collecting chloramine	4 min.
Fraction of chloramine solution transferred to conductivity cell	0.75
Volume of chloramine solution transferred to conductivity cell	60 ml.
Time of transferring chloramine solution to conductivity cell	7:34
Time of transferring hydrazine solution to conductivity cell	7:38
Time of diluting near the volumetric line with liquid ammonia	7:44
Volume of cell contents at the end of the rate measurement	70.99 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.75 ml.
Volume of cell contents after adding hydrazine and mixing	71.74 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	105.30

Table 15 Experiment Number R9⁻⁷⁵

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
4.0	295	100	29,500	3.39
12.0	295	100	29,500	3.39
20.5	280	100	28,000	3.57
26.0	225	100	22,500	4.44
31.0	198	100	19,800	5.05
40.0	137	100	13,700	7.30
40.5	132	100	13,200	7.58
41.0	127	100	12,700	7.87
43.0	112	100	11,200	8.93
44.8	97	100	9,700	10.31
47.0	75	100	7,500	13.33
49.0	53	100	5,300	18.87
52.0	32	100	3,200	31.25
54.0	213	10	2,130	46.95
56.0	168	10	1,680	59.52
58.0	147	10	1,470	68.08
61.5	132	10	1,320	75.76
64.0	123	10	1,230	81.30
68.0	120	10	1,200	83.33
73.8	112	10	1,120	89.28
82.0	110	10	1,100	90.91
102.0	107	10	1,070	93.46
115.0	105	10	1,050	95.24
128.0	105	10	1,050	95.24
142.0	104	10	1,040	96.15
Add 0.75 ml. N ₂ H ₄				
	95	10	950	105.26
	95	10	950	105.26
	95.	10	950	105.26
	93	10	930	107.53
	93	10	930	107.53
	93	10	930	107.53
	95	10	950	105.26

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R9-75

Fig.40

Table 16 Experiment Number R 10⁻⁷⁵

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which a solution of hydrazine was added.

Date of the measurement	June 30, 1955
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0107 g.
Difference in height of the two limbs of the chlorine manometer expressed in mm. of sulfuric acid	120 mm.
Time spent in wasting chloramine	12 min.
Time spent in collecting chloramine	4.25 min.
Fraction of chloramine solution transferred to conductivity cell	0.64
Volume of chloramine solution transferred to conductivity cell	45 ml.
Time of transferring chloramine solution to conductivity cell	5:18
Time of transferring hydrazine solution to conductivity cell	5:25
Time of diluting near the volumetric line with liquid ammonia	5:30
Volume of cell contents at the end of the rate measurement	71.29 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.7 ml.
Volume of cell contents after adding hydrazine and mixing	71.99 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	103.09

Table 16 Experiment Number R10⁻⁷⁵

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
1.0	2,250	10	22,500	4.44
3.0	2,330	10	23,300	4.29
5.0	2,320	10	23,200	4.31
8.0	2,320	10	23,200	4.31
11.0	2,300	10	23,000	4.35
15.0	2,300	10	23,000	4.35
21.0	2,270	10	22,700	4.40
28.0	2,240	10	22,400	4.46
37.0	2,200	10	22,000	4.54
50.0	2,100	10	21,000	4.76
60.0	1,970	10	19,700	5.08
73.0	1,750	10	17,500	5.71
80.0	1,680	10	16,800	5.95
90.0	1,435	10	14,350	6.97
101.0	1,240	10	12,400	8.06
109.0	1,100	10	11,000	9.09
119.0	950	10	9,500	10.53
127.0	857	10	8,570	11.67
134.0	790	10	7,900	12.66
143.0	697	10	6,970	14.35
151.0	630	10	6,300	15.87
158.0	580	10	5,800	17.24
166.0	523	10	5,230	19.12
168.0	515	10	5,150	19.42
181.0	448	10	4,480	22.32
189.0	412	10	4,120	24.27
198.0	378	10	3,780	26.46
204.0	360	10	3,600	27.78
217.0	319	10	3,190	31.35
227.0	300	10	3,000	33.33
234.0	282	10	2,820	35.46
244.0	263	10	2,630	38.02
252.0	249	10	2,490	40.16
257.0	243	10	2,430	41.15
270.0	225	10	2,250	44.44
283.0	214	10	2,140	46.73
293.0	210	10	2,100	47.62
306.0	197	10	1,970	50.76
318.0	190	10	1,900	52.63
332.0	187	10	1,870	53.48

Table 16 Experiment Number R10⁻⁷⁵ (cont.)

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
358.0	182	10	1,820	54.94
377.0	183	10	1,830	54.64
390.0	180	10	1,800	55.56
400.0	182	10	1,820	54.94
Add 0.7 ml. N ₂ H ₄				
	97	10	970	103.09
	97	10	970	103.09
	97	10	970	103.09

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R10⁻⁷⁵

Fig. 41

Table 17 Experiment Number R 11-75

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which a weighed quantity of hydrazine was added.

Date of the measurement	July 3, 1955
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0165 g.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	15 min.
Time spent in collecting chloramine	4 min.
Fraction of chloramine solution transferred to conductivity cell	0.66
Volume of chloramine solution transferred to conductivity cell	44 ml.
Time of transferring chloramine solution to conductivity cell	1:55
Time of transferring hydrazine solution to conductivity cell	1:59
Time of diluting near the volumetric line with liquid ammonia	2:02
Volume of cell contents at the end of the rate measurement	71.47 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.7 ml.
Volume of cell contents after adding hydrazine and mixing	72.17 ml.
Final conductivity reading in reciprocal ohmsx10 ⁵ after adding hydrazine and mixing	99.01

No graph prepared for this experiment, since thermostat overheated. Data only useful for stoichiometry measurement.

Table 17 Experiment Number R11-75

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
2.0	1850	10	18500	5.40
3.5	1770	10	17700	5.65
8.0	240	10	2400	41.67
8.8	138	10	1380	72.46
10.0	122	10	1220	81.97
11.0	121	10	1210	82.64
14.0	121	10	1210	82.64
17.0	120	10	1200	83.33
25.0	120	10	1200	83.33
add 0.7 ml. N ₂ H ₄				
	102	10	1020	98.04
	101	10	1010	99.01

Table 18 Experiment Number R 12⁻⁷⁵

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which a weighed quantity of hydrazine was added.

Date of the measurement	July 19, 1955
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0221 g.
Difference in height of the two limbs of the chlorine manometer expressed in mm. of sulfuric acid	130 mm.
Time spent in wasting chloramine	12 min.
Time spent in collecting chloramine	4 min.
Fraction of chloramine solution transferred to conductivity cell	0.83
Volume of chloramine solution transferred to conductivity cell	50 ml.
Time of transferring chloramine solution to conductivity cell	4:05
Time of transferring hydrazine solution to conductivity cell	4:12
Time of diluting near the volumetric line with liquid ammonia	4:15
Volume of cell contents at the end of the rate measurement	72.47 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	1.0 ml.
Volume of cell contents after adding hydrazine and mixing	72.25 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	158.73

Table 18 Experiment Number R12-75

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
1.0	1,300	10	13,000	7.69
3.0	1,250	10	12,500	8.00
5.0	1,255	10	12,550	7.97
9.0	1,285	10	12,850	7.78
11.0	1,242	10	12,420	8.05
14.0	1,110	10	11,100	9.01
16.0	940	10	9,400	10.64
17.0	840	10	8,400	11.90
19.0	650	10	6,500	15.38
20.6	533	10	5,330	18.76
22.0	410	10	4,100	24.39
24.6	257	10	2,570	38.91
26.6	156	10	1,560	64.10
28.7	128	10	1,280	78.12
30.0	120	10	1,200	83.33
32.0	110	10	1,100	90.91
34.0	110	10	1,100	90.91
36.0	103	10	1,030	97.09
41.0	100	10	1,000	100.00
53.0	98	10	980	102.04
64.0	96	10	960	104.17
69.0	96	10	960	104.17
Add 0.8 ml. N ₂ H ₄				
	63	10	630	158.73

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R12-75

Fig.42

-155-
Table 19 Experiment Number R 13-75

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which a weighed quantity of hydrazine was added.

Date of the measurement	July 28, 1955
Conductivity cell number	3
Exact bath temperature	-74.3° C.
Weight in grams of added hydrazine	0.0109 g.
Difference in height of the two limbs of the chlorine manometer expressed in mm. of sulfuric acid	114 mm.
Time spent in wasting chloramine	12 min.
Time spent in collecting chloramine	3.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.88
Volume of chloramine solution transferred to conductivity cell	35 ml.
Time of transferring chloramine solution to conductivity cell	8:25
Time of transferring hydrazine solution to conductivity cell	8:30
Time of diluting near the volumetric line with liquid ammonia	8:35
Volume of cell contents at the end of the rate measurement	70.99 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.4 ml.
Volume of cell contents after adding hydrazine and mixing	71.39 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	120.48

Table 19 Experiment Number R13-75

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
3.0	1,580	10	15,800	6.33
6.0	1,580	10	15,800	6.33
14.0	1,590	10	15,900	6.29
20.0	1,580	10	15,800	6.33
24.0	1,570	10	15,700	6.37
30.0	1,570	10	15,700	6.37
42.0	1,540	10	15,400	6.49
52.0	1,500	10	15,000	6.67
70.0	1,480	10	14,800	6.76
82.0	1,445	10	14,450	6.92
97.0	1,420	10	14,200	7.04
108.0	1,400	10	14,000	7.14
121.0	1,375	10	13,750	7.27
132.0	1,310	10	13,100	7.63
143.0	1,255	10	12,550	7.97
159.0	1,160	10	11,600	8.62
162.0	1,135	10	11,350	8.81
171.0	1,073	10	10,730	9.32
185.0	1,042	10	10,420	9.60
199.0	1,000	10	10,000	10.00
235.0	773	10	7,730	12.94
260.0	633	10	6,330	15.80
284.0	530	10	5,300	18.87
304.0	457	10	4,570	21.88
350.0	315	10	3,150	31.75
366.0	307	10	3,070	32.67
394.0	269	10	2,690	37.17
427.0	237	10	2,370	42.19
458.0	217	10	2,170	46.08
482.0	205	10	2,050	48.78
508.0	197	10	1,970	50.76
570.0	185	10	1,850	54.05
596.0	177	10	1,770	56.50
633.0	175	10	1,750	57.14
651.0	175	10	1,750	57.14
679.0	174	10	1,740	57.47
697.0	174	10	1,740	57.47
Add 0.4 ml. N ₂ H ₄				
	83	10	830	120.48

Fig.43

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R13-75

Table 20 Experiment Number R 14⁻⁷⁵

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which weighed quantities of hydrazine and ammonium chloride were added.

Date of the measurement	August 6, 1955
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0115 g.
Weight in grams of added ammonium chloride	0.0079 g.
Difference in height of the two limbs of the chlorine manometer expressed in mm. sulfuric acid	120 mm.
Time spent in wasting chloramine	12 min.
Time spent in collecting chloramine	3.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.73
Volume of chloramine solution transferred to conductivity cell	40 ml.
Time of transferring chloramine solution to conductivity cell	7:18
Time of transferring solution of hydrazine and ammonium chloride to conductivity cell	7:22
Time of diluting near the volumetric line with liquid ammonia	7:24
Volume of cell contents at the end of the rate measurement	71.39 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.6 ml.
Volume of cell contents after adding hydrazine and mixing	71.99 ml.
Final conductivity reading in reciprocal ohms $\times 10^5$ after adding hydrazine and mixing	133.33

Table 20 Experiment Number R14-75

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
2.0	442	10	4,420	22.62
3.0	445	10	4,450	22.47
6.0	455	10	4,550	21.98
9.0	380	10	3,800	26.32
11.0	340	10	3,400	29.41
12.5	300	10	3,000	33.33
16.0	247	10	2,470	40.48
18.0	221	10	2,210	45.25
22.0	195	10	1,950	51.28
27.0	181	10	1,810	55.25
35.0	163	10	1,630	61.35
43.0	157	10	1,570	63.69
50.3	151	10	1,510	66.22
58.3	148	10	1,480	67.57
67.0	143	10	1,430	69.93
81.5	143	10	1,430	69.93
93.0	141	10	1,410	70.92
110.0	138	10	1,380	72.46
126.0	137	10	1,370	72.99
158.0	137	10	1,370	72.99
185.0	137	10	1,370	72.99
Add 0.6 ml. N ₂ H ₄				
	75	10	750	133.33
	76	10	760	131.58

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER RI4-75

Fig. 44

Table 21 Experiment Number R 15-75

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of measurement	August 31, 1955
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0121 g.
Weight in grams of added ammonium chloride	0.0067 g.
Difference in height of the two limbs of the chlorine manometer expressed in mm. of sulfuric acid	120 mm.
Time spent in wasting chloramine	9 min.
Time spent in collecting chloramine	3.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.80
Volume of chloramine solution transferred to conductivity cell	40 ml.
Time of transferring chloramine solution to conductivity cell	4:43
Time of transferring solution of hydrazine and ammonium chloride to conductivity cell	4:50
Time of diluting near the volumetric line with liquid ammonia	4:55
Volume of cell contents at the end of the rate measurement	71.49 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.6 ml.
Volume of cell contents after adding hydrazine and mixing	71.89 ml.
Final conductivity reading in reciprocal ohms $\times 10^5$ after adding hydrazine and mixing	114.94

Table 21 Experiment Number R15⁻⁷⁵

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
2.0	583	10	5,830	17.15
4.0	597	10	5,970	16.75
6.0	600	10	6,000	16.67
9.5	600	10	6,000	16.67
10.0	600	10	6,000	16.67
11.5	300	10	3,000	33.33
12.0	255	10	2,550	39.22
12.75	223	10	2,230	44.84
13.0	220	10	2,200	45.45
13.75	192	10	1,920	52.08
15.0	175	10	1,750	57.14
16.3	167	10	1,670	59.88
17.3	163	10	1,630	61.35
23.0	155	10	1,550	64.52
28.0	153	10	1,530	65.36
42.0	152	10	1,520	65.79
56.0	150	10	1,500	66.67
Add 0.6 ml. N ₂ H ₄				
	87	10	870	114.94

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R15-75

Fig. 45

Table 10 Experiment Number R 16⁻⁷⁵

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which weighed quantities of hydrazine and ammonium chloride were added.

Date of the measurement	Sept. 2, 1955
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0104g.
Weight in grams of added ammonium chloride	0.0111g.
Difference in height of the two limbs of the chlorine monometer expressed in mm. of sulfuric acid	120 mm.
Time spent in wasting chloramine	10 min.
Time spent in collecting chloramine	3.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.80
Volume of chloramine solution transferred to conductivity cell	40 ml.
Time of transferring chloramine solution to conductivity cell	4:30
Time of transferring solution of hydrazine and ammonium chloride to conductivity cell	4:34
Time of diluting near the volumetric line with liquid ammonia	4:39
Volume of cell contents at the end of the rate measurement	74.36 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.6 ml.
Volume of cell contents after adding hydrazine and mixing	77.22 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	158.73

Table 22 Experiment Number R16-75

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
2.0	333	10	3,330	30.03
4.0	337	10	3,370	29.67
5.0	340	10	3,400	29.41
7.0	342	10	3,420	29.24
9.5	342	10	3,420	29.24
11.0	340	10	3,400	29.41
14.0	342	10	3,420	29.24
18.0	338	10	3,380	29.58
20.0	310	10	3,100	32.26
20.5	300	10	3,000	33.33
21.0	295	10	2,950	33.90
22.0	280	10	2,800	35.71
23.0	268	10	2,680	37.31
24.0	258	10	2,580	38.76
25.0	248	10	2,480	40.32
28.0	218	10	2,180	45.87
33.0	190	10	1,900	52.63
37.0	179	10	1,790	55.86
41.0	163	10	1,630	61.35
47.0	155	10	1,550	64.52
53.0	148	10	1,480	67.57
58.0	147	10	1,470	68.03
71.0	141	10	1,410	70.92
76.0	141	10	1,410	70.92
90.0	140	10	1,400	71.43
98.0	138	10	1,380	72.46
114.0	136	10	1,360	73.53
133.0	133	10	1,330	75.19
157.0	133	10	1,330	75.19
184.0	131	10	1,310	76.34
198.0	132	10	1,320	75.76
209.0	132	10	1,320	75.76
214.0	132	10	1,320	75.76
218.0	132	10	1,320	75.76

Add 0.6 ml. N₂H₄

62.5	10	625	160.00
63	10	630	158.73

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT
NUMBER R16-75 Fig.46

Table 23 Experiment Number R 17-75

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which weighed quantities of hydrazine and ammonium chloride were added.

Date of the measurement	Sept. 8, 1955
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0106 g.
Weight in grams of added ammonium chloride	0.0094
Difference in height of the two limbs of the chlorine manometer expressed in mm. of sulfuric acid	120 mm.
Time spent in wasting chloramine	13 min.
Time spent in collecting chloramine	2.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.89
Volume of chloramine solution transferred to conductivity cell	40 ml.
Time of transferring chloramine solution to conductivity cell	2:07
Time of transferring solution of hydrazine and ammonium chloride to conductivity cell	2:14
Time of diluting near the volumetric line with liquid ammonia	2:18
Volume of cell contents at the end of the rate measurement	71.29 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 m.
Volume of cell contents after adding hydrazine and mixing	71.79 ml.
Final conductivity reading in redprocal ohmx10 ⁵ after adding hydrazine and mixing	121.95

Table 23 Experiment Number R17⁻⁷⁵

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
2.0	365	10	3,650	27.40
4.0	373	10	3,730	26.81
6.0	370	10	3,700	27.03
7.5	370	10	3,700	27.03
9.0	372	10	3,720	26.88
12.0	370	10	3,700	27.03
14.0	370	10	3,700	27.03
15.0	367	10	3,670	27.25
18.0	360	10	3,600	27.78
21.3	342	10	3,420	29.24
23.0	328	10	3,280	30.49
25.0	312	10	3,120	32.05
27.3	292	10	2,920	34.25
30.0	273	10	2,730	36.63
33.0	254	10	2,540	39.37
37.0	230	10	2,300	43.48
42.5	208	10	2,080	48.08
45.0	200	10	2,000	50.00
50.0	182	10	1,820	54.94
53.0	177	10	1,770	56.50
57.0	168	10	1,680	59.52
65.0	160	10	1,600	62.50
74.0	150	10	1,500	66.67
87.0	142	10	1,420	70.42
92.0	143	10	1,430	69.93
104.0	137	10	1,370	72.99
112.0	137	10	1,370	72.99
134.0	135	10	1,350	74.07
158.0	138	10	1,380	72.46
166.0	137	10	1,370	72.99
Add 0.5 ml. N ₂ H ₄				
	82	10	820	121.95
	83	10	830	120.48
	82	10	820	121.95

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R17-75

Fig.47

Table 24 Experiment Number R 18⁻⁷⁵

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which weighed quantities of hydrazine and ammonium chloride were added.

Date of the measurement	Sept. 14, 1955
Conductivity cell number	3
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0103
Weight in grams of added ammonium chloride	0.0144
Difference in height of the two limbs of the chlorine monometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	10 min.
Time spent in collecting chloramine	2.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.90
Volume of chloramine solution transferred to conductivity cell	45 ml.
Time of transferring chloramine solution to conductivity cell	3:11
Time of transferring solution of hydrazine and ammonium chloride to conductivity cell	3:18
Time of diluting near the volumetric line with liquid ammonia	3:21
Volume of cell contents at the end of the rate measurement	71.09 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	71.59 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	147.06

Table 24 Experiment Number R18-75

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
2.0	265	10	2,650	37.74
3.0	267	10	2,670	37.45
4.0	267	10	2,670	37.45
7.5	262	10	2,620	38.17
9.0	261	10	2,610	38.31
11.0	264	10	2,640	37.88
14.0	261	10	2,610	38.31
16.5	261	10	2,610	38.31
21.5	253	10	2,530	39.52
23.0	251	10	2,510	39.84
25.0	247	10	2,470	40.48
28.0	238	10	2,380	42.02
30.0	225	10	2,250	44.44
32.5	217	10	2,170	46.08
35.0	210	10	2,100	47.62
37.0	201	10	2,010	49.75
40.0	192	10	1,920	52.08
44.0	183	10	1,830	54.64
47.0	178	10	1,780	56.18
52.0	166	10	1,660	60.24
57.0	159	10	1,590	62.89
62.0	152	10	1,520	65.79
65.0	150	10	1,500	66.67
69.0	147	10	1,470	68.03
73.0	143	10	1,430	69.93
84.0	139	10	1,390	71.94
88.0	134	10	1,340	74.63
100.0	131	10	1,310	76.34
119.5	128	10	1,280	78.12
138.0	127	10	1,270	78.74
160.0	126	10	1,260	79.36
179.0	123	10	1,230	81.30
183.0	126	10	1,260	79.36
206.0	124	10	1,240	80.64
217.0	124	10	1,240	80.64
Add 0.5 ml. N ₂ H ₄				
	68.5	10	685	145.98
	69	10	690	144.93
	68	10	680	147.06

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT
NUMBER R18-75

Fig. 48

Table 25 Experiment Number R 19⁻⁷⁵

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which a weighed quantity of hydrazine was added.

Date of measurements	March 14, 1956
Conductivity cell number	4
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0104 g.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	13 min.
Time spent in collecting chloramine	4 min.
Fraction of chloramine solution transferred to conductivity cell	0.83
Volume of chloramine solution transferred to conductivity cell	50 ml.
Time of transferring chloramine solution to conductivity cell	3:20
Time of transferring hydrazine solution to conductivity cell	3:25
Time of diluting near the volumetric line with liquid ammonia	3:30
Volume of cell contents at the end of the rate measurement	59.0 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	1.0 ml.
Volume of cell contents after adding hydrazine and mixing	60.0 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	102.04

Table 25 Experiment Number R19-75

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
4.0	128	100	12,800	7.81
7.0	93	100	9,300	10.75
7.5	62	100	6,200	16.13
8.5	38	100	3,800	26.32
9.0	30	100	3,000	33.33
10.0	23	100	2,300	43.48
12.0	167	10	1,670	59.88
13.0	155	10	1,550	64.52
15.0	152	10	1,520	65.79
18.0	157	10	1,570	63.69
19.0	151	10	1,510	66.22
23.0	150	10	1,500	66.67
25.0	151	10	1,510	66.22
30.0	148	10	1,480	67.57
40.0	150	10	1,500	66.67
53.0	149	10	1,490	67.11
Add 1.0 ml. N ₂ H ₄				
	98	10	980	102.04

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT
NUMBER R19-75

Fig.49

Table 26 Experiment Number R 20-75

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution initially composed of chloramine dissolved in anhydrous ammonia to which a weighed quantity of hydrazine was added.

Date of the measurement	March 16, 1956
Conductivity cell number	4
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0108 g.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	94 mm.
Time spent in wasting chloramine	15 min.
Time spent in collecting chloramine	3.25 min.
Fraction of chloramine solution transferred to conductivity cell	0.80
Volume of chloramine solution transferred to conductivity cell	40 ml.
Time of transferring chloramine solution to conductivity cell	12:24
Time of transferring solution of hydrazine to conductivity cell	12:40
Time of diluting near the volumetric line with liquid ammonia	12:43
Volume of cell contents at the end of the rate measurement	71.69 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	72.09 ml.
Final conductivity reading in reciprocal ohms $\times 10^3$ after adding hydrazine and mixing	505.05

Table 26 Experiment Number R20-75

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
5.0	290	100	29,000	3.45
7.0	290	100	29,000	3.45
9.0	278	100	27,800	3.60
12.0	290	100	29,000	3.45
14.0	295	100	29,500	3.39
17.0	300	100	30,000	3.33
22.0	298	100	29,800	3.36
27.0	298	100	29,800	3.36
32.0	272	100	27,200	3.68
33.5	242	100	24,200	4.13
35.0	239	100	23,900	4.18
37.0	240	100	24,000	4.17
39.0	238	100	23,800	4.20
42.0	2,220	10	22,200	4.50
42.5	2,070	10	20,700	4.83
43.5	1,900	10	19,000	5.26
44.0	1,790	10	17,900	5.59
45.0	1,650	10	16,500	6.06
46.0	1,503	10	15,030	6.65
47.5	1,440	10	14,400	6.94
50.0	1,440	10	14,400	6.94
53.0	1,420	10	14,200	7.04
54.0	1,335	10	13,350	7.49
55.0	1,260	10	12,600	7.94
55.5	1,200	10	12,000	8.33
56.8	1,100	10	11,000	9.09
57.5	1,058	10	10,580	9.45
58.5	983	10	9,830	10.17
59.0	948	10	9,480	10.55
60.0	883	10	8,830	11.32
61.5	760	10	7,600	13.16
62.5	670	10	6,700	14.92
63.5	567	10	5,670	17.64
65.0	442	10	4,420	22.62
66.0	373	10	3,730	26.81
67.0	309	10	3,090	32.36
68.5	268	10	2,680	37.31
70.0	240	10	2,400	46.67
71.5	230	10	2,300	43.48
72.5	220	10	2,200	45.45
74.0	212	10	2,120	47.17
76.0	208	10	2,080	48.08

Table 26 Experiment Number R20-75 (cont.)

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
78.0	202	10	2,020	49.50
81.5	200	10	2,000	50.00
85.0	198	10	1,980	50.50
90.0	196	10	1,960	51.02
96.0	197	10	1,970	50.76
110.0	196	10	1,960	51.02
115.0	197	10	1,970	50.76
129.0	197	10	1,970	50.76
165.0	195	10	1,950	51.28
Add 0.5 ml. N ₂ H ₄				
	197	10	1,970	50.76
	198	10	1,980	50.50

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT
NUMBER R20-75

Fig.50

Table 27 Experiment Number R 22-75

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia to which a weighed quantity of hydrazine was added.

Date of the measurement	March 23, 1956
Conductivity cell number	4
Exact bath temperature	-74.3°C.
Weight in grams of added hydrazine	0.0102 g.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	100 mm.
Time spent in wasting chloramine	13 min.
Time spent in collecting chloramine	3.25 min.
Fraction of chloramine solution transferred to conductivity cell	0.91
Volume of chloramine solution transferred to conductivity cell	50 ml.
Time of transferring chloramine solution to conductivity cell	1:28
Time of transferring solution of hydrazine to conductivity cell	1:33
Time of diluting near the volumetric line with liquid ammonia	1:37
Volume of cell contents at the end of the rate measurement	72.09 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.6 ml.
Volume of cell contents after adding hydrazine and mixing	72.24 ml.
Final conductivity reading in reciprocal ohms $\times 10^5$ after adding hydrazine and mixing	120.48

Table 27 Experiment Number R22-75

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
0.0	103	100	10,300	9.71
4.0	105	100	10,500	9.52
6.0	108	100	10,800	9.26
8.0	110	100	11,000	9.09
10.0	112	100	11,200	8.93
15.0	111	100	11,100	9.01
17.0	108	100	10,800	9.26
18.0	103	100	10,300	9.71
19.0	97	100	9,700	10.31
20.0	93	100	9,300	10.75
21.0	87	100	8,700	11.49
22.5	80	100	8,000	12.50
23.0	75	100	7,500	13.33
24.75	645	10	6,450	15.50
25.5	593	10	5,930	16.86
26.75	520	10	5,200	19.23
28.0	447	10	4,470	22.37
29.0	400	10	4,000	25.00
30.0	370	10	3,700	27.03
31.0	330	10	3,300	30.30
32.5	300	10	3,000	33.33
33.5	275	10	2,750	36.36
35.0	258	10	2,580	38.76
36.0	248	10	2,480	40.32
38.0	232	10	2,320	43.10
39.5	220	10	2,200	45.45
41.0	213	10	2,130	46.95
43.0	210	10	2,100	47.62
46.0	202	10	2,020	49.50
52.0	190	10	1,900	52.63
59.0	184	10	1,840	54.35
72.5	177	10	1,770	56.50
79.5	174	10	1,740	57.47
91.5	173	10	1,730	57.80
102.0	172	10	1,720	58.14
113.0	171	10	1,710	58.48
121.0	171	10	1,710	58.48
137.0	179	10	1,700	58.82
148.0	170	10	1,700	58.82
Add 0.6 ml. N ₂ H ₄				
	83	10	830	120.48
	82	10	820	121.95
	83	10	830	120.48

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT
NUMBER R22-75

Fig. 51

Table 28 Experiment Number R 23-60

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of measurement	March 27, 1956
Conductivity cell number	4
Exact bath temperature	-60.4°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	100 mm.
Time spent in wasting chloramine	12 min.
Time spent in collecting chloramine	3.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.93
Volume of chloramine solution transferred to conductivity cell	65 ml.
Time of transferring chloramine solution to conductivity cell	11:47
Time of diluting near the volumetric line with liquid ammonia	11:55
Volume of cell contents at the end of the rate measurement	71.89 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	72.89 ml.
Final conductivity reading in reciprocal ohms $\times 10^5$ after adding hydrazine and mixing	176.99

Table 28 Experiment Number R23-60

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
0.0	880	10	8,800	11.36
0.3	870	10	8,700	11.49
2.5	840	10	8,400	11.90
4.5	835	10	8,350	11.98
5.3	835	10	8,350	11.98
7.0	833	10	8,330	12.00
8.8	832	10	8,320	12.02
13.0	820	10	8,200	12.20
15.0	813	10	8,130	12.30
18.0	793	10	7,930	12.61
21.0	780	10	7,800	12.82
22.5	764	10	7,640	13.09
24.3	757	10	7,570	13.21
26.3	743	10	7,430	13.46
28.0	737	10	7,370	13.57
31.0	727	10	7,270	13.76
35.0	707	10	7,070	14.14
38.0	687	10	6,870	14.56
41.0	675	10	6,750	14.81
45.0	660	10	6,600	15.15
48.3	652	10	6,520	15.34
53.0	639	10	6,390	15.65
58.0	618	10	6,180	16.18
63.5	598	10	5,980	16.72
66.0	593	10	5,930	16.86
72.0	575	10	5,750	17.39
75.0	567	10	5,670	17.64
83.0	547	10	5,470	18.28
87.5	538	10	5,380	18.59
95.0	522	10	5,220	19.16
103.0	505	10	5,050	19.80
111.5	491	10	4,910	20.37
116.0	478	10	4,780	20.92
125.0	462	10	4,620	21.64
137.5	447	10	4,470	22.37
146.0	437	10	4,370	22.88
160.3	415	10	4,150	24.10
168.3	404	10	4,040	24.75
179.0	390	10	3,900	25.64
187.0	386	10	3,860	25.91
195.0	380	10	3,800	26.32
209.0	363	10	3,630	27.55
223.0	351	10	3,510	28.49
235.0	342	10	3,420	29.24

Table 28 Experiment Number R23-60 (cont.)

Elapsed time in minutes	Dial	Factor	Ohms	Mhos x 10 ⁵
257.0	323	10	3,230	30.96
276.0	317	10	3,170	31.54
292.0	304	10	3,040	32.89
307.0	296	10	2,960	33.78
315.0	287	10	2,870	34.84
342.0	274	10	2,740	36.50
363.0	260	10	2,600	38.46
390.5	255	10	2,550	39.22
404.3	248	10	2,480	40.32
427.0	240	10	2,400	41.67
452.0	237	10	2,370	42.19
470.0	232	10	2,320	43.10
489.0	223	10	2,230	44.84
530.0	214	10	2,140	46.73
Add 0.5 ml. N ₂ H ₄				
	56.5	10	565	176.99
	57	10	570	175.44
	573	1	573	174.52
	567	1	567	176.37
	56.5	10	565	176.99

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R23-60

Fig. 52

Table 29 Experiment Number R 24-60

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	April 13, 1956
Conductivity cell number	4
Exact bath temperature	-60.4°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	10 min.
Time spent in collecting chloramine	3.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.83
Volume of chloramine solution transferred to conductivity cell	50 ml.
Time of transferring chloramine solution to conductivity cell	:143
Time of diluting near the volumetric line with liquid ammonia	1:48
Volume of cell contents at the end of the rate measurement	72.79 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	73.29 ml.
Final conductivity reading in reciprocal ohms x 10^5 after adding hydrazine and mixing	164.20

Table 29 Experiment Number R24⁻⁶⁰

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
0	-	-		
2	962	10	9,620	10.40
4	963	10	9,630	10.38
6	960	10	9,600	10.42
7.5	950	10	9,500	10.53
10.0	930	10	9,300	10.75
12.0	917	10	9,170	10.90
15.0	900	10	9,000	11.11
17.5	885	10	8,850	11.30
20.5	867	10	8,670	11.53
23.0	847	10	8,470	11.81
27.0	826	10	8,260	12.11
29.0	814	10	8,140	12.28
33.0	793	10	7,930	12.61
37.0	773	10	7,730	12.94
40.0	755	10	7,550	13.24
43.0	743	10	7,430	13.46
49.5	713	10	7,130	14.02
57.0	685	10	6,850	14.60
62.5	670	10	6,700	14.92
67.0	655	10	6,550	15.27
76.0	625	10	6,250	16.01
83.0	608	10	6,080	16.45
88.0	592	10	5,920	16.89
98.0	567	10	5,670	17.64
102.0	562	10	5,620	17.79
103.5	558	10	5,580	17.92
112.0	540	10	5,400	18.52
121.5	527	10	5,270	18.98
127.5	513	10	5,130	19.49
137.0	495	10	4,950	20.20
145.0	483	10	4,830	20.70
151.0	477	10	4,770	20.96
161.0	458	10	4,580	21.83
177.5	442	10	4,420	22.62
185.0	437	10	4,370	22.88
199.0	417	10	4,170	23.98
217.0	398	10	3,980	25.12
236.0	378	10	3,780	26.46
239.0	374	10	3,740	26.74

Table 29 Experiment Number R24⁻⁶⁰ (cont).

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
263.0	357	10	3,570	28.01
269.0	350	10	3,500	28.57
296.0	336	10	3,360	29.76
321.0	320	10	3,200	31.25
351.5	310	10	3,100	32.26
367.0	294	10	2,940	34.01
391.0	283	10	2,830	35.34
398.0	210	10	2,100	47.62
399.0	205	10	2,050	48.78
400.0	190	10	1,900	52.63
401.0	1870	1	1,870	53.48
402.0	1800	1	1,800	55.56
403.0	1750	1	1,750	57.14
405.0	1680	1	1,680	59.52
406.0	1650	1	1,650	60.61
408.0	1600	1	1,600	62.50
409.0	1575	1	1,575	63.49
411.0	1560	1	1,560	64.10
414.0	1515	1	1,515	66.01
417.0	1495	1	1,495	66.89
418.0	1470	1	1,470	68.03
420.5	1455	1	1,455	68.73
424.0	1435	1	1,435	69.69
426.5	1427	1	1,427	70.08
429.0	1420	1	1,420	70.42
430.5	1403	1	1,403	71.28
432.5	1400	1	1,400	71.43
435.0	1390	1	1,390	71.94
446.0	1375	1	1,375	72.73
448.2	1365	1	1,365	73.26
454.0	1347	1	1,347	74.24
462.5	1335	1	1,335	74.91
483.7	1303	1	1,303	76.74
500.0	1270	1	1,270	78.74
521.0	1240	1	1,240	80.64
548.0	1212	1	1,212	82.30
559.0	1195	1	1,195	83.68
583.0	1188	1	1,188	84.18
add 0.5 ml. N ₂ H ₄				
	610	1		163.93
	608	1		164.47
	609	1		164.20

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R24-60

Fig. 53

Table 30 Experiment Number R 25-60

Rate Measurement Data

Data given in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of measurement	April 17, 1956
Conductivity cell number	4
Exact bath temperature	-60.4°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	15 min.
Time spent in collecting chloramine	3.5 min.
Fraction of chloramine solution transferred to conductivity cell	.80
Volume of chloramine solution transferred to conductivity cell	40 ml.
Time of transferring chloramine solution to conductivity cell	1:35
Time of diluting near the volumetric line with liquid ammonia	1:40
Volume of cell contents at the end of the rate measurement	72.46 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonia chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	72.46 ml.
Final conductivity reading in reciprocal ohms x 10 ⁹ after adding hydrazine and mixing	188.67
Cell contents boiled over during final mixing.	

Table 30 Experiment Number 25⁻⁶⁰

Elapsed time in min mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
0.0	-	-		
3.0	800	10	8,000	12.50
5.0	740	10	7,400	13.51
6.5	683	10	6,830	14.64
8.0	665	10	6,650	15.04
10.0	650	10	6,500	15.38
12.5	637	10	6,370	15.70
19.0	619	10	6,190	16.16
26.0	613	10	6,130	16.31
33.0	597	10	5,970	16.75
36.0	583	10	5,830	17.15
42.0	563	10	5,630	17.67
48.0	547	10	5,470	18.28
56.0	523	10	5,230	19.12
63.0	510	10	5,100	19.61
66.5	498	10	4,980	20.08
75.0	488	10	4,880	20.49
86.0	467	10	4,670	21.41
90.5	460	10	4,600	21.74
101.0	440	10	4,400	22.73
103.0	437	10	4,370	22.88
114.0	422	10	4,220	23.70
120.5	412	10	4,120	24.27
125.3	407	10	4,070	24.57
136.5	393	10	3,930	25.50
150.0	380	10	3,800	26.32
164.0	367	10	3,670	27.25
178.5	350	10	3,500	28.57
186.5	345	10	3,450	28.98
199.0	332	10	3,320	30.12
214.0	325	10	3,250	30.77
221.0	318	10	3,180	31.45
231.5	312	10	3,120	32.05
245.0	300	10	3,000	33.33
263.0	289	10	2,890	34.60
271.0	288	10	2,880	34.72
277.0	284	10	2,840	35.21
293.0	278	10	2,780	35.97
308.5	268	10	2,680	37.31
320.0	264	10	2,640	37.88
332.0	260	10	2,600	38.46
341.0	257	10	2,571	38.90

Table 30 Experiment Number 25⁻⁶⁰ (cont)

Elapsed time in min mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
352.0	250	10	2,500	40.00
361.0	248	10	2,480	40.32
371.5	244	10	2,440	40.98
385.0	239	10	2,390	41.84
398.0	234	10	2,340	42.74
407.0	233	10	2,330	42.92
416.0	230	10	2,300	43.48
436.0	227	10	2,270	44.05
447.0	223	10	2,230	44.84
455.0	220	10	2,200	45.45
469.0	216	10	2,160	46.30
481.5	211	10	2,110	47.39
499.5	209	10	2,090	47.85
511.0	206	10	2,060	48.54
530.0	202	10	2,020	49.50
544.0	198	10	1,980	50.50
549.0	1980	1	1,980	50.50
555.0	1965	1	1,965	50.89
564.0	1920	1	1,920	52.08
580.0	1885	1	1,885	53.05
592.0	1865	1	1,865	53.62
606.0	1835	1	1,835	54.50
635.0	1780	1	1,780	56.18
659.0	1760	1	1,760	56.82
675.0	1730	1	1,730	57.80
692.0	1690	1	1,690	59.17
710.0	1670	1	1,670	59.88
739.0	1635	1	1,635	61.16
Add 0.5 ml. N ₂ H ₄				
	527	1	527	189.75
	530	1	530	188.68
	532	1	532	187.97

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R25-60
Fig. 54

Table 31 Experiment Number R 26-60

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	April 19, 1956
Conductivity cell number	4
Exact bath temperature	-60.4°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	13 min.
Time spent in collecting chloramine	3.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.93
Volume of chloramine solution transferred to conductivity cell	65 ml.
Time of transferring chloramine solution to conductivity cell	9:50
Time of diluting near the volumetric line with liquid ammonia	9:53
Volume of cell contents at the end of the rate measurement	72.51 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	72.56 ml.
Final conductivity reading in reciprocal ohms x 10^5 after adding hydrazine and mixing	195.31

Table 31 Experiment Number R26⁻⁶⁰

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
0.0	593	10	5,930	16.86
2.0	593	10	5,930	16.86
3.0	594	10	5,940	16.84
6.0	575	10	5,750	17.39
9.5	568	10	5,680	17.60
13.3	555	10	5,550	18.02
20.0	540	10	5,400	18.52
24.5	533	10	5,330	18.76
27.0	512	10	5,120	19.53
30.0	510	10	5,100	19.61
38.3	500	10	5,000	20.00
43.0	492	10	4,920	20.32
51.5	473	19	4,730	21.14
52.5	472	10	4,720	21.19
59.5	460	10	4,600	21.74
65.3	453	10	4,530	22.08
72.0	443	10	4,430	22.57
81.5	428	10	4,280	23.36
95.3	405	10	4,050	24.69
105.4	397	10	3,970	25.19
115.6	383	10	3,830	26.11
132.5	368	10	3,680	27.17
142.3	360	10	3,600	27.78
151.0	350	10	3,500	28.57
165.5	343	10	3,430	29.16
174.0	331	10	3,310	30.21
183.0	328	10	3,280	30.49
197.0	318	10	3,180	31.45
210.7	311	10	3,110	32.15
219.0	304	10	3,040	32.89
241.5	292	10	2,920	34.25
253.8	287	10	2,870	34.84
269.3	278	10	2,780	35.97
285.7	269	10	2,690	37.17
304.0	263	10	2,630	38.02
323.6	253	10	2,530	39.52
341.0	247	10	2,470	40.48
363.0	240	10	2,400	41.67
380.0	236	10	2,360	42.37
395.0	231	10	2,310	43.29
417.0	225	10	2,250	44.44
436.0	219	10	2,190	45.60

Table 31 Experiment Number R26⁻⁶⁰ (cont).

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
452.0	213	10	2,130	46.95
476.0	209	10	2,090	47.85
494.0	206	10	2,060	48.54
523.0	1980	1	1,980	50.50
534.5	1970	1	1,970	50.76
558.0	1925	1	1,925	51.95
574.5	1875	1	1,875	53.33
592.5	1850	1	1,850	54.05
602.5	1830	1	1,830	54.64
621.7	1785	1	1,785	56.02
635.5	1770	1	1,770	56.50
651.0	1740	1	1,740	57.47
681.0	1695	1	1,695	59.00
703.5	1670	1	1,670	59.90
737.5	1617	1	1,617	61.84
749.0	1600	1	1,600	62.50
771.0	1580	1	1,580	63.29
801.3	1555	1	1,555	64.30
815.0	1535	1	1,535	65.15
826.0	1520	1	1,520	65.79
850.0	1493	1	1,493	66.98
865.4	1483	1	1,483	67.43
Add 0.5 ml. N H				
	2 4			
	511	1	511	195.69
	513	1	513	194.93

Fig. 55
PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R26-60

Table 32 Experiment Number 27⁻⁶⁰

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of measurement	April 24, 1956
Conductivity cell number	4
Exact bath temperature	-60.4°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	13 min.
Time spent in collecting chloramine	3 min.
Fraction of chloramine solution transferred to conductivity cell	0.91
Volume of chloramine solution transferred to conductivity cell	50 ml.
Time of transferring chloramine solution to conductivity cell	10:50
Time of diluting near the volumetric line with liquid ammonia	10:53
Volume of cell contents at the end of the rate measurement	72.36 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	72.56 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	194.93

Table 32 Experiment Number R27-60

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
0.0	-	-		
2.5	800	10	8.000	12.50
3.3	778	10	7,780	12.85
4.5	779	10	7,790	12.84
7.5	757	10	7,570	13.21
10.3	747	10	7,470	13.39
14.0	720	10	7,200	13.89
20.7	698	10	6,980	14.33
23.7	682	10	6,820	14.66
27.7	662	10	6,620	15.10
31.3	647	10	6,470	15.46
41.8	607	10	6,070	16.47
45.3	595	10	5,950	16.81
51.0	580	10	5,800	17.24
59.8	554	10	5,540	18.05
68.0	528	10	5,280	18.94
80.3	506	10	5,060	19.76
93.0	481	10	4,810	20.79
100.3	467	10	4,670	21.41
110.3	451	10	4,510	22.17
116.3	441	10	4,410	22.68
128.8	423	10	4,230	23.64
134.0	418	10	4,180	23.92
141.7	405	10	4,050	24.69
152.0	393	10	3,930	25.44
165.5	378	10	3,780	26.46
177.5	368	10	3,680	27.17
199.5	348	10	3,480	28.74
212.0	334	10	3,340	29.94
224.8	323	10	3,230	30.96
236.5	313	10	3,130	31.95
251.0	308	10	3,080	32.47
264.5	298	10	2,980	33.56
281.0	291	10	2,910	34.36
294.0	281	10	2,810	35.59
309.5	277	10	2,770	36.10
325.0	267	10	2,670	37.45
347.7	258	10	2,580	38.76
360.0	256	10	2,560	39.06
376.0	248	10	2,480	40.32
393.5	242	10	2,420	41.32

Table 32 Experiment Number R27-60 (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
408.7	233	10	2,330	42.92
421.5	233	10	2,330	42.92
437.0	228	10	2,280	43.86
460.0	222.5	10	2,225	44.94
480.2	215	10	2,150	46.51
491.5	211.5	10	2,115	47.28
509.0	209	10	2,090	47.85
528.0	204	10	2,040	49.02
529.7	2045	1	2,045	48.90
552.5	1985	1	1,985	50.38
571.3	1935	1	1,935	51.68
593.7	1915	1	1,915	52.22
606.0	1880	1	1,880	53.19
628.5	1835	1	1,835	54.50
664.3	1780	1	1,780	56.18
682.0	1740	1	1,740	57.47
709.8	1700	1	1,700	58.82
739.0	1670	1	1,670	59.88
761.0	1640	1	1,640	60.98
784.3	1615	1	1,615	61.92
803.0	1600	1	1,600	62.50
823.0	1570	1	1,570	63.69
846.0	1550	1	1,550	64.52
863.3	1520	1	1,520	65.79
872.0	1510	1	1,510	66.22
881.0	1507	1	1,507	66.36
Add 0.5 ml. N ₂ H ₄				
	507	1	507	175.44
	518	1	518	193.05
	513	1	513	194.93
	512	1	512	195.31
	514	1	514	194.55
	515	1	515	194.17

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R27-60
Fig. 56

Table 33 Experiment Number R 28⁻⁶⁰

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	April 27, 1956
Conductivity cell number	4
Exact bath temperature	-60.4°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	15 min.
Time spent in collecting chloramine	2.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.91
Volume of chloramine solution transferred to conductivity cell	50 ml.
Time of transferring chloramine solution to conductivity cell	10:35
Time of diluting near the volumetric line with liquid ammonia	10:40
Volume of cell contents at the end of the rate measurement	72.36 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.4 ml.
Volume of cell contents after adding hydrazine and mixing	72.36 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	144.51

Table 33 Experiment Number R28-60

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
2.0	1480	10	14,800	6.76
4.5	1441	10	14,410	6.94
8.2	1378	10	13,780	7.26
11.5	1321	10	13,210	7.57
15.0	1282	10	12,820	7.80
16.8	1260	10	12,600	7.94
19.3	1223	10	12,230	8.18
23.5	1187	10	11,870	8.42
27.7	1145	10	11,450	8.73
33.5	1087	10	10,870	9.20
40.3	1037	10	10,370	9.64
42.3	1023	10	10,230	9.78
45.0	1003	10	10,030	9.97
50.0	968	10	9,680	10.33
55.7	927	10	9,270	10.79
60.3	898	10	8,980	11.14
68.2	--	--		
73.5	836	10	8,360	11.96
78.3	815	10	8,150	12.27
88.2	770	10	7,700	12.98
98.3	737	10	7,370	13.57
102.0	728	10	7,280	13.74
108.2	700	10	7,000	14.28
115.0	683	10	6,830	14.64
120.2	667	10	6,670	14.99
126.0	648	10	6,480	15.43
131.2	637	10	6,370	15.70
137.2	626	10	6,260	15.97
141.3	613	10	6,130	16.31
147.0	599	10	5,990	16.69
153.3	590	10	5,900	16.95
161.5	567	10	5,670	17.61
170.0	554	10	5,540	18.05
183.3	533	10	5,330	18.76
196.4	514	10	5,140	19.46
206.5	493	10	4,930	20.28
223.3	477	10	4,770	20.96
240.2	457	10	4,570	21.88
253.3	440	10	4,400	22.72
266.0	429	10	4,290	23.31
275.5	418	10	4,180	23.92

Table 33 Experiment Number R28-60 (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
287.5	412	10	4,120	24.27
300.0	398	10	3,980	25.17
317.0	387.5	10	3,875	25.81
329.5	378	10	3,780	26.46
345.2	370	10	3,700	27.03
346.7	370	10	3,700	27.03
367.5	353	10	3,530	28.33
389.3	339	10	3,390	29.50
416.7	327	10	3,270	30.58
432.2	322	10	3,220	31.06
459.6	308	10	3,080	32.47
475.5	304	10	3,040	32.89
500.0	293	10	2,930	34.13
527.5	283	10	2,830	35.34
550.0	277	10	2,770	36.10
570.8	271	10	2,710	36.90
600.0	262	10	2,620	38.17
624.7	254	10	2,540	39.37
646.0	250	10	2,500	40.00
680.0	240	10	2,400	41.67
702.5	237	10	2,370	42.19
740.5	228	10	2,280	43.86
756.3	227	10	2,270	44.05
773.5	224	10	2,240	44.64
775.0	223	10	2,230	44.84
779.0	221	10	2,210	45.25
783.0	221	10	2,210	45.25

Add 0.4 ml. N₂H₅

696	1	696	143.68
685	1	685	145.98
687	1	687	145.56
693	1	693	144.30
688	1	688	145.35
693	1	693	144.30
697	1	697	143.47
698	1	698	143.27
695	1	695	143.88
693	1	693	144.30

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R28-60

Fig. 57

Table 34 Experiment Number R 29-50

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	May 12, 1956
Conductivity cell number	4
Exact bath temperature	-50.6°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	18 min.
Time spent in collecting chloramine	3.25 min.
Fraction of chloramine solution transferred to conductivity cell	0.87
Volume of chloramine solution transferred to conductivity cell	48 ml.
Time of transferring chloramine solution to conductivity cell	11:31
Time of diluting near the volumetric line with liquid ammonia	11:32
Volume of cell contents at the end of the rate measurement	69.89 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	70.09 ml.
Final conductivity reading in reciprocal ohms $\times 10^5$ after adding hydrazine and mixing	201.21

Table 34 Experiment Number R29-50

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance, mhos x 10 ³
2.5	700	10	7,000	14.28
3.0	660	10	6,600	15.15
4.0	640	10	6,400	15.62
5.7	620	10	6,200	16.13
7.0	600	10	6,000	16.67
8.0	585	10	5,850	17.09
10.0	568	10	5,680	17.60
12.0	545	10	5,450	18.35
14.0	527	10	5,270	18.98
16.7	500	10	5,000	20.00
18.7	490	10	4,900	20.41
22.0	460	10	4,600	21.74
23.5	454	10	4,540	22.03
28.0	422	10	4,220	23.70
31.3	407	10	4,070	24.57
38.2	376	10	3,760	26.60
43.3	358	10	3,580	27.93
48.5	338	10	3,380	29.58
52.7	323	10	3,230	30.96
56.0	318	10	3,180	31.45
60.0	305	10	3,050	32.79
65.0	293	10	2,930	34.13
72.8	278	10	2,780	35.97
80.3	262	10	2,620	38.17
84.5	256	10	2,560	39.06
92.0	244	10	2,440	40.98
101.0	230	10	2,300	43.48
107.7	224	10	2,240	44.04
114.5	213	10	2,130	46.94
123.0	207	10	2,070	48.31
130.0	200	10	2,000	50.00
135.0	197	10	1,970	50.76
140.5	1920	1	1,920	52.08
146.5	1870	1	1,870	53.48
163.2	1765	1	1,765	56.66
170.8	1715	1	1,715	58.31
175.3	1680	1	1,680	59.52
185.0	1635	1	1,635	61.16
190.0	1605	1	1,605	62.30
204.7	1535	1	1,535	65.15
214.0	1515	1	1,515	66.01

Table 34 Experiment Number R29-50 (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
229.8	1435	1	1,435	69.69
244.0	1395	1	1,395	71.68
269.0	1315	1	1,315	76.04
287.3	1270	1	1,270	78.74
298.7	1241	1	1,241	80.58
320.3	1187	1	1,187	84.24
347.5	1140	1	1,140	87.72
366.5	1105	1	1,105	90.50
393.0	1060	1	1,060	94.34
418.0	1027	1	1,027	97.37
442.0	997	1	997	100.30
463.0	975	1	975	102.56
486.3	954	1	954	104.82
506.2	927	1	927	107.87
539.7	897	1	897	111.48
542.0	895	1	895	111.86
569.0	872	1	872	114.68
597.0	845	1	845	118.34
617.5	835	1	835	119.76
626.7	827	1	827	120.92
635.7	815	1	815	122.70
Add 0.5 ml. N ₂ H ₄				
	497	1	497	201.21
	498	1	498	200.80
	497	1	497	201.21

Fig. 58
 PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R29-50

Table 35 Experiment Number R 30-50

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	April 15, 1956
Conductivity cell number	4
Exact bath temperature	-50.6°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	112 mm.
Time spent in wasting chloramine	21 min.
Time spent in collecting chloramine	3 min.
Fraction of chloramine solution transferred to conductivity cell	0.91
Volume of chloramine solution transferred to conductivity cell	50 ml.
Time of transferring chloramine solution to conductivity cell	10:58
Time of diluting near the volumetric line with liquid ammonia	11:00
Volume of cell contents at the end of the rate measurement	72.34 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml
Volume of cell contents after adding hydrazine and mixing	72.39 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	205.76

Table 35 Experiment Number R30-50

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	Bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
1.5	900	10	9,000	11.11
2.0	865	10	8,650	11.56
2.5	850	10	8,500	11.76
3.5	825	10	8,250	12.12
4.5	800	10	8,000	12.50
5.2	787	10	7,870	12.71
6.2	763	10	7,630	13.11
7.7	725	10	7,250	13.79
8.8	705	10	7,050	14.18
10.3	678	10	6,780	14.75
11.8	658	10	6,580	15.20
14.3	618	10	6,180	16.18
16.7	584	10	5,840	17.12
19.0	558	10	5,580	17.92
21.2	536	10	5,360	18.66
24.0	503	10	5,030	19.88
27.2	477	10	4,770	20.96
30.3	455	10	4,550	21.98
34.0	428	10	4,280	23.36
36.3	415	10	4,150	24.10
40.8	394	10	3,940	25.38
46.2	372	10	3,720	26.88
47.7	364	10	3,640	27.47
52.0	350	10	3,500	28.57
55.0	337	10	3,370	29.67
56.8	330	10	3,300	30.30
59.0	325	10	3,250	30.77
66.8	304	10	3,040	32.89
72.8	290	10	2,900	34.48
77.7	281	10	2,810	35.59
82.0	270	10	2,700	37.04
86.2	260	10	2,600	38.46
91.0	252	10	2,520	39.68
95.0	247	10	2,470	40.49
97.8	243	10	2,430	41.15
105.3	233	10	2,330	42.92
115.0	220	10	2,200	45.45
121.5	209	10	2,090	47.85
133.0	120	10	1,200	83.33
135.0	115	10	1,150	86.96
137.7	110	10	1,100	90.91

Table 35 Experiment Number R30⁵⁰ (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
144.3	103	10	1,030	97.09
146.7	100	10	1,000	100.00
148.3	987	1	987	101.32
155.0	955	1	955	104.71
162.0	931	1	931	107.41
170.0	910	1	910	109.89
178.0	883	1	883	113.25
184.8	865	1	865	115.61
193.0	847	1	847	118.06
198.0	835	1	835	119.76
202.8	827	1	827	120.92
212.3	805	1	805	124.22
224.0	793	1	793	126.10
230.5	778	1	778	128.53
238.0	767	1	767	130.38
247.0	755	1	755	132.45
253.0	747	1	747	133.87
262.6	739	1	739	135.32
266.5	734	1	734	136.34
273.5	723	1	723	138.31
285.0	715	1	715	139.86
303.5	694	1	694	144.09
318.7	682	1	682	146.63
321.0	677	1	677	147.71
337.5	662	1	662	151.06
368.5	642	1	642	155.77
386.0	630	1	630	158.173
395.5	626	1	626	159.74
411.8	615	1	615	162.60
427.5	607	1	607	164.74
444.8	602	1	602	166.11
464.5	595	1	595	168.07
487.5	583	1	583	171.53
505.0	580	1	580	172.41
521.0	575	1	575	173.91
535.0	567	1	567	176.37
566.5	561	1	561	178.25
590.3	557	1	557	179.33
614.8	547	1	547	182.82
634.3	545	1	545	183.49
654.5	540	1	540	185.18

Table 35 Experiment Number R30⁵⁰ (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity bridge dial reading	multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
670.0	540	1	540	185.18
715.0	535	1	535	186.92
739.0	517	1	517	193.42
745.0	527	1	527	189.75
747.3	525	1	525	190.48
749.5	526	1	526	190.11
Add 0.5 ml. N ₂ H ₄				
	486	1	486	205.76
	487	1	487	205.34

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R30-50

Fig. 59

Table 36 Experiment Number R 31-50

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	May 17, 1956
Conductivity cell number	4
Exact bath temperature	-50.6°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	13 min.
Time spent in collecting chloramine	3 min.
Fraction of chloramine solution transferred to conductivity cell	0.83
Volume of chloramine solution transferred to conductivity cell	50 ml.
Time of transferring chloramine solution to conductivity cell	11:37
Time of diluting near the volumetric line with liquid ammonia	11:38
Volume of cell contents at the end of the rate measurement	72.29 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonia chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	72.42 ml.
Final conductivity reading in reciprocal ohms x 10^5 after adding hydrazine and mixing	182.82

Table 36 Experiment Number R31-50

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
1.5	870	10	8,700	11.49
2.3	855	10	8,550	11.70
3.0	830	10	8,300	12.05
4.0	810	10	8,100	12.34
5.3	780	10	7,800	12.82
6.5	860	10	7,600	13.16
7.5	742	10	7,420	13.48
8.5	723	10	7,230	13.83
10.2	700	10	7,000	14.28
11.5	677	10	6,770	14.77
13.2	654	10	6,540	15.29
16.3	609	10	6,090	16.42
19.0	593	10	5,930	16.86
21.0	573	10	5,730	17.45
23.0	553	10	5,530	18.08
25.2	533	10	5,330	18.76
27.7	515	10	5,150	19.42
30.0	499	10	4,990	20.04
32.9	478	10	4,780	20.92
36.7	458	10	4,580	21.83
40.7	433	10	4,330	23.09
47.8	400	10	4,000	25.00
55.0	374	10	3,740	26.74
58.8	360	10	3,600	27.78
65.3	340	10	3,400	29.41
68.2	332	10	3,320	30.12
73.7	320	10	3,200	31.25
79.3	310	10	3,100	32.26
87.0	293	10	2,930	34.13
92.8	283	10	2,830	35.34
101.0	270	10	2,700	37.04
111.0	253	10	2,530	39.53
120.7	241	10	2,410	41.49
131.8	230	10	2,300	43.48
149.5	213	10	2,130	46.95
157.3	207	10	2,070	48.31
168.0	1980	1	1,980	50.50
178.7	1910	1	1,910	52.36
190.3	1845	1	1,845	54.20
208.3	1745	1	1,745	57.31

Table 36 Experiment Number R31-50 (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
219.9	1690	1	1,690	59.17
229.5	1650	1	1,650	60.61
239.3	1615	1	1,615	61.92
253.5	1545	1	1,545	64.72
267.0	1500	1	1,500	66.67
278.5	1460	1	1,460	68.49
288.0	1425	1	1,425	70.18
299.8	1397	1	1,397	71.58
314.0	1361	1	1,361	73.48
327.3	810	1	810	123.46
328.3	765	1	765	130.72
329.3	742	1	765	134.77
330.5	715	1	715	139.86
332.2	700	1	700	142.86
334.2	678	1	678	147.49
336.3	675	1	675	148.15
338.0	659	1	659	151.74
343.7	647	1	647	154.56
355.0	639	1	639	156.49
366.0	633	1	633	157.98
382.0	627	1	627	159.49
411.5	620	1	620	161.30
429.0	615	1	615	162.60
453.8	607	1	607	164.74
484.5	605	1	605	165.29
520.5	598	1	598	167.22
551.5	595	1	595	168.07
579.3	590	1	590	169.49
610.5	590	1	590	169.41
643.0	588	1	588	170.97
651.0	587	1	587	170.36
Add 0.50 ml. N ₂ H ₄				
	547	1	547	182.82

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R31-50

Fig. 60

Table 37 Experiment Number R 32-50

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of measurement	May 21, 1956
Conductivity cell number	4
Exact bath temperature	-50.6°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	13 min.
Time spent in collecting chloramine	3 min.
Fraction of chloramine solution transferred to conductivity cell	0.92
Volume of chloramine solution transferred to conductivity cell	55 ml.
Time of transferring chloramine solution to conductivity cell	11:28
Time of diluting near the volumetric line with liquid ammonia	11:29
Volume of cell contents at the end of the rate measurement	72.09 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	72.16 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	180.50

The column headed "Conc., NH₄Cl, moles/liter x 10⁵" was obtained using the equation - Conc. of NH₄Cl, moles/liter x 10⁵ = $\text{antilog}(\frac{1}{a} \log \text{reciprocal resistance} - \frac{b}{a})$ where $(\frac{1}{a}) = 1.3432$ and $(\frac{b}{a}) = 2.0531$

Table 37 Experiment Number R32⁻⁵⁰

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity bridge dial multi- read- plying ing factor	Resis- tance ohms	Reciprocal resistance mhos x 10 ⁵	Conc. NH ₄ Cl moles/ liter x 10 ⁵
2.0	823	10	8,230	62.2
3.0	800	10	8,000	64.6
4.0	779	10	7,790	67.0
5.7	740	10	7,400	72.695
8.2	702	10	7,020	77.0
10.0	678	10	6,780	79.6
12.0	645	10	6,450	86.3
13.3	635	10	6,350	88.1
15.0	607	10	6,070	94.0
17.0	593	10	5,930	96.6
21.5	547	10	5,470	107.7
24.2	527	10	5,270	113.2
27.0	505	10	5,050	119.9
29.5	488	10	4,880	125.5
32.8	470	10	4,700	132.0
36.5	460	10	4,600	138.4
39.5	432	10	4,320	147.9
42.0	420	10	4,200	153.6
45.5	405	10	4,050	161.3
47.3	397	10	3,970	168.7
49.5	390	10	3,900	169.7
52.0	380	10	3,800	171.3
56.0	367	10	3,670	184.1
57.5	360	10	3,600	188.9
61.8	347	10	3,470	202.1
68.0	330	10	3,300	216.2
73.5	317	10	3,170	228.2
82.0	299	10	2,990	242.5
89.3	288	10	2,880	264.0
96.8	273	10	2,730	279.0
105.0	261	10	2,610	291.0
110.7	253	10	2,530	303.4
118.0	243	10	2,430	319.4
126.0	234	10	2,340	337.0
130.0	230	10	2,300	344.8
141.0	220	10	2,200	366.0
145.7	218	10	2,180	370.6
151.5	210	10	2,100	389.7
158.5	207	10	2,070	397.3

Table 37 Experiment Number R32⁻⁵⁰ (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity bridge dial multi- read- plying ing factor		Resis- tance ohms	Reciprocal resistance mhos x 10 ⁵	Conc. NH ₄ Cl moles/ liter x 10 ⁵
171.3	1965	1	1,965	50.89	426.1
176.3	1930	1	1,930	51.81	436.4
184.2	1870	1	1,870	53.48	455.3
191.7	1830	1	1,830	54.64	468.8
205.5	1765	1	1,765	56.66	492.1
226.3	1665	1	1,665	60.06	532.2
237.0	1615	1	1,615	61.92	554.4
247.0	1575	1	1,575	63.49	573.4
260.0	1525	1	1,525	65.57	598.8
266.0	1499	1	1,499	66.71	612.9
274.7	1470	1	1,470	68.03	629.2
280.0	1460	1	1,460	68.49	634.9
285.0	1443	1	1,443	69.30	645.0
292.5	1420	1	1,420	70.42	659.0
297.5	1405	1	1,405	71.17	668.5
301.0	1330	1	1,330	75.19	719.6
301.7	1245	1	1,245	80.32	786.5
302.5	1090	1	1,090	91.74	940.2
303.0	990	1	990	101.01	1053.2
303.7	947	1	947	105.60	1136.4
304.2	885	1	885	112.99	1241.6
304.7	850	1	850	117.65	1313.1
305.3	822	1	822	121.65	1373.4
306.2	779	1	779	128.37	1476.4
307.0	755	1	755	132.45	1540.0
308.5	733	1	733	136.42	1602.2
309.6	710	1	710	140.84	1703.0
310.5	713	1	713	140.25	1662.7
312.0	700	1	700	142.86	1704.5
313.0	695	1	695	143.88	1720.7
314.0	690	1	690	144.93	1737.8
316.0	682	1	682	146.63	1764.8
318.5	680	1	680	147.06	1772.8
323.7	673	1	673	148.60	1796.8
332.0	665	1	665	150.38	1826.0
337.0	663	1	663	150.83	1833.2
345.2	660	1	660	151.52	1867.2
362.0	654	1	654	152.90	1867.2
372.0	650	1	650	153.85	1882.8
406.3	646	1	646	154.80	1898.4
448.5	642	1	642	155.76	1914.3

Table 37 Experiment Number R32-50 (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity bridge dial read- ing	multi- plying factor	Resis- tance ohms	Reciprocal resistance mhos x 10 ⁵	Conc. NH ₄ Cl moles/ liter x 10 ⁵
450.0	647	1	647	154.56	1894.5
453.0	645	1	645	155.04	1902.4
456.0	644	1	644	155.28	1906.3
484.0	640	1	640	156.26	1922.2
510.5	639	1	639	156.49	1926.2
567.7	635	1	635	157.48	1942.7
570.0	635	1	635	157.48	1942.7
599.0	633	1	633	157.98	1951.3
601.0	633	1	633	157.98	1951.3
628.5	630	1	630	158.73	1963.4
630.0	633	1	633	157.98	1951.3
632.0	630	1	630	158.74	1963.4
656.0	627	1	627	159.49	1975.9
664.0	625	1	625	160.00	1980.4
667.0	626	1	626	159.74	1980.0
670.0	625	1	625	160.00	1980.4
Add 0.5 ml. N ₂ H ₄					
	555	1	555	180.18	2327.9
	554	1	554	180.50	2333.3
	553	1	553	180.83	2395.0

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R32-50

Fig.61

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R32-50

Fig. 62

Table 38 Experiment Number R 33-50

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	May 23, 1956
Conductivity cell number	4
Exact bath temperature	-50.6°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	12 min.
Time spent in collecting chloramine	3 min.
Volume of chloramine solution transferred to conductivity cell	55 ml.
Fraction of chloramine solution transferred to conductivity cell	0.92
Time of transferring chloramine solution to conductivity cell	11:19
Time of diluting near the volumetric line with liquid ammonia	11:21
Volume of cell contents at the end of the rate measurement	72.36 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	72.42 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	170.94

Table 38 Experiment Number R33-50

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
1.0	1060	10	10,600	9.43
2.0	1028	10	10,280	9.73
3.0	995	10	9,950	10.05
4.5	970	10	9,700	10.30
6.0	895	10	8,950	11.17
7.8	857	10	8,570	11.67
9.3	818	10	8,180	12.22
11.0	785	10	7,850	12.74
12.8	755	10	7,550	13.24
15.0	718	10	7,180	13.93
16.3	700	10	7,000	14.28
18.5	673	10	6,730	14.86
21.0	641	10	6,410	15.60
23.2	618	10	6,180	16.18
25.7	587	10	5,870	17.04
29.0	565	10	5,650	17.70
31.9	540	10	5,400	18.52
35.3	516	10	5,160	19.38
39.3	490	10	4,900	20.41
43.3	470	10	4,700	21.28
46.0	457	10	4,570	21.88
48.3	443	10	4,430	22.57
50.7	430	10	4,300	23.26
53.2	418	10	4,180	23.92
56.0	408	10	4,080	24.51
60.3	391	10	3,910	25.58
63.2	383	10	3,830	26.11
66.3	371	10	3,710	26.95
69.0	360	10	3,600	27.78
73.3	353	10	3,530	28.33
75.6	343	10	3,430	29.15
79.5	332	10	3,320	30.12
85.5	321	10	3,210	31.15
89.7	313	10	3,130	31.95
94.7	303	10	3,030	33.00
101.0	292	10	2,920	34.25
106.7	282	10	2,820	35.46
112.8	272	10	2,720	36.76
124.7	258	10	2,580	38.76
130.5	249	10	2,490	40.16
135.0	243	10	2,430	41.15
144.7	234	10	2,340	42.74

Table 38 Experiment Number R33-50 (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
149.7	229	10	2,290	43.67
155.8	224	10	2,240	44.64
160.0	219	10	2,190	45.66
167.5	213	10	2,130	46.95
173.2	210	10	2,100	47.62
180.3	2060	1	2,060	48.54
188.2	2000	1	2,000	50.00
193.7	1980	1	1,980	50.50
203.0	1915	1	1,915	52.22
209.8	1870	1	1,870	53.48
217.5	1830	1	1,830	54.64
219.5	1820	1	1,820	54.94
230.5	1770	1	1,770	56.50
235.7	1745	1	1,745	57.31
245.8	1695	1	1,695	59.00
258.0	1640	1	1,640	60.98
270.5	1585	1	1,585	63.09
285.0	1530	1	1,530	65.36
295.3	1505	1	1,505	66.44
311.2	1460	1	1,460	68.49
322.2	1430	1	1,430	69.93
330.3	1410	1	1,410	70.92
341.3	1385	1	1,385	72.20
351.8	1363	1	1,363	73.37
364.7	1335	1	1,335	74.91
373.3	1315	1	1,315	76.04
388.3	1287	1	1,287	77.70
398.7	1265	1	1,265	79.05
426.3	1220	1	1,220	81.97
438.2	1202	1	1,202	83.19
454.0	1177	1	1,177	84.96
467.0	1165	1	1,165	85.84
479.5	1150	1	1,150	86.95
496.5	1125	1	1,125	88.89
529.7	1085	1	1,085	92.16
542.5	1075	1	1,075	93.02
573.0	1042	1	1,042	95.97
587.0	1025	1	1,025	97.56
598.0	1011	1	1,011	98.91
635.5	987	1	987	101.32
663.0	965	1	965	103.63

Table 38 Experiment Number R33⁻⁵⁰ (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
689.5	947	1	947	105.60
701.0	940	1	940	106.38
714.5	930	1	930	107.53
735.3	918	1	918	108.93
746.7	907	1	907	110.25
766.0	900	1	900	111.11
777.0	895	1	895	111.86
Add 0.5 ml. N ₂ H ₄				
	585	1	585	170.94

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R33-50

Fig. 63

Table 39 Experiment Number R 34-50

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	May 27, 1956
Conductivity cell number	4
Exact bath temperature	-50.6°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	115 mm.
Time spent in wasting chloramine	14 min.
Time spent in collecting chloramine	3 min.
Fraction of chloramine solution transferred to conductivity cell	0.92
Volume of chloramine solution transferred to conductivity cell	60 ml.
Time of transferring chloramine solution to conductivity cell	12:02
Time of diluting near the volumetric line with liquid ammonia	12:03
Volume of cell contents at the end of the rate measurement	71.29 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.7 ml.
Volume of cell contents after adding hydrazine and mixing	71.49 ml.
Final conductivity reading in reciprocal ohms x 10^5 after adding hydrazine and mixing	216.45

Table 39 Experiment Number R34-50

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
1.3	605	10	6,050	16.53
2.4	585	10	5,850	17.09
3.5	580	10	5,800	17.24
4.7	560	10	5,600	17.86
6.3	545	10	5,450	18.35
7.3	537	10	5,370	18.62
9.0	520	10	5,200	19.23
10.2	505	10	5,050	19.80
12.0	488	10	4,880	20.49
13.7	478	10	4,780	20.92
15.6	463	10	4,630	21.60
18.2	440	10	4,400	22.73
22.2	410	10	4,100	24.39
26.0	397	10	3,970	25.19
29.5	379	10	3,790	26.38
32.8	367	10	3,670	27.25
36.0	352	10	3,520	28.41
40.0	337	10	3,370	29.67
42.3	330	10	3,300	30.30
46.2	320	10	3,200	31.25
49.5	310	10	3,100	32.26
52.5	302	10	3,020	33.11
56.0	294	10	2,940	34.01
59.2	285	10	2,850	35.09
65.3	273	10	2,730	36.63
68.7	266	10	2,660	37.59
71.8	260	10	2,600	38.46
75.2	254	10	2,540	39.37
81.3	244	10	2,440	40.98
87.3	236	10	2,360	42.37
93.5	227	10	2,270	44.05
100.0	125	10	1,250	80.00
101.0	122	10	1,220	81.97
102.7	1167	1	1,167	85.69
104.0	1145	1	1,145	87.34
107.0	1120	1	1,120	89.28
110.2	1103	1	1,103	90.66
113.5	1083	1	1,083	92.34
117.3	1058	1	1,058	94.52
127.7	1020	1	1,020	98.04
130.7	1007	1	1,007	99.30

Table 39 Experiment Number R34⁻⁵⁰ (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
136.8	983	1	983	101.73
143.0	961	1	961	104.05
149.5	935	1	935	106.95
155.0	917	1	917	109.05
161.2	902	1	902	110.86
167.2	885	1	885	112.99
173.5	867	1	867	115.34
180.0	855	1	855	116.96
186.0	840	1	840	119.05
193.0	825	1	825	121.21
196.2	823	1	823	121.51
202.5	807	1	807	123.92
209.0	793	1	793	126.10
221.7	775	1	775	129.03
230.0	760	1	760	131.58
242.2	743	1	743	134.59
255.2	727	1	727	137.55
261.3	710	1	710	140.84
267.5	707	1	707	141.44
289.0	690	1	690	144.93
297.5	680	1	680	147.06
303.0	677	1	677	147.71
324.7	673	1	673	148.59
334.7	665	1	665	150.38
354.0	660	1	660	151.52
381.5	653	1	653	153.14
383.7	653	1	653	153.14
409.0	645	1	645	155.04
414.2	642	1	642	155.76
436.7	640	1	640	156.25
443.0	637	1	637	156.98
455.0	635	1	635	157.48
477.2	630	1	630	158.73
481.0	630	1	630	158.73
Add 0.7 ml. N ₂ H ₄				
	463	1	463	215.98
	462	1	462	216.45
	460	1	460	217.39
	462	1	462	216.45

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT
NUMBER R34-50

Fig. 64

Table 40 Experiment Number R 35-50

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	May 29, 1956
Conductivity cell number	4
Exact bath temperature	-50.6°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	13 min.
Time spent in collecting chloramine	3.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.93
Volume of chloramine solution transferred to conductivity cell	65 ml.
Time of transferring chloramine solution to conductivity cell	12:07
Time of diluting near the volumetric line with liquid ammonia	12:08
Volume of cell contents at the end of the rate measurement	71.49 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	71.39ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	249.38

Table 40 Experiment Number R35-50

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
2.0	535	10	5,350	18.69
4.8	505	10	5,050	19.80
6.0	493	10	4,930	20.29
7.3	473	10	4,730	21.14
9.3	462	10	4,620	21.64
10.8	447	10	4,470	22.37
12.2	440	10	4,400	22.73
13.8	422	10	4,220	23.70
15.0	415	10	4,150	24.10
16.0	406	10	4,060	24.63
17.5	400	10	4,000	25.00
19.0	388	10	3,880	25.77
21.0	379	10	3,790	26.38
22.5	368	10	3,680	27.17
24.0	363	10	3,630	27.55
26.0	351	10	3,510	28.49
29.0	338	10	3,380	29.58
30.8	330	10	3,300	30.30
33.0	325	10	3,250	30.77
34.5	320	10	3,200	31.25
36.2	314	10	3,140	31.85
38.2	305	10	3,050	32.79
40.3	300	10	3,000	33.33
44.5	287	10	2,870	34.84
48.8	275	10	2,750	36.36
51.3	270	10	2,700	37.04
55.0	262	10	2,620	38.17
58.8	253	10	2,530	39.52
62.7	248	10	2,480	40.32
65.7	241	10	2,410	41.49
69.5	234	10	2,340	42.74
72.5	230	10	2,300	43.48
76.0	222	10	2,220	45.04
78.7	210	10	2,190	45.66
81.8	217	10	2,170	46.08
84.0	219	10	2,100	47.62
88.4	203	10	2,030	49.26
96.5	193	10	1,930	51.81
101.3	1875	1	1,875	53.33
106.8	1830	1	1830	54.64
108.3	1801	1	1,801	55.52

Table 40 Experiment Number R35⁻⁵⁰ (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
111.2	1780	1	1,780	56.18
117.5	1730	1	1,730	57.80
122.3	1695	1	1,695	59.00
126.2	1665	1	1,665	60.06
133.3	1615	1	1,615	61.92
137.6	1585	1	1,585	63.09
140.4	1565	1	1,565	63.90
144.3	1535	1	1,535	65.15
147.6	1515	1	1,515	66.01
152.5	1487	1	1,487	67.25
156.5	1465	1	1,465	68.26
165.0	1425	1	1,425	70.18
168.0	1410	1	1,410	70.92
171.2	1397	1	1,397	71.58
180.8	1355	1	1,355	73.80
186.7	1333	1	1,333	75.02
198.8	1285	1	1,285	77.82
206.0	1255	1	1,255	79.68
211.2	1237	1	1,237	80.84
216.0	1220	1	1,220	81.91
227.0	1185	1	1,185	84.39
234.0	1165	1	1,165	85.84
243.5	1140	1,	1,140	87.72
248.3	1122	1	1,122	89.13
257.2	1100	1	1,100	90.91
270.2	1075	1	1,075	93.02
281.5	1045	1	1,045	95.69
288.0	1017	1	1,017	98.33
297.0	1007	1	1,007	99.30
313.8	985	1	985	101.52
320.0	967	1	967	103.41
326.6	960	1	960	104.17
332.0	955	1	955	104.71
338.3	940	1	940	106.38
345.0	930	1	930	107.53
352.3	915	1	915	109.29
364.3	905	1	905	110.50
378.2	881	1	881	113.51
384.5	867	1	867	115.34
393.0	861	1	861	116.14
410.0	839	1	839	119.19

Table 40 Experiment Number R35⁻⁵⁰ (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
414.0	700	1	700	142.86
414.7	683	1	683	146.41
415.2	645	1	645	155.04
416.0	605	1	605	165.29
416.7	565	1	565	177.00
417.2	543	1	543	184.16
417.6	520	1	520	192.31
418.1	505	1	505	198.02
418.5	495	1	495	202.02
419.0	477	1	477	209.64
419.6	470	1	470	212.76
420.0	463	1	463	215.98
420.8	450	1	450	222.22
421.7	441	1	441	226.76
423.0	433	1	433	230.95
424.3	425	1	425	235.29
425.4	422	1	422	236.96
426.8	420	1	420	238.09
428.5	417	1	417	239.80
434.3	415	1	415	240.96
453.0	410	1	410	243.90
464.7	411	1	411	243.31
498.8	409	1	409	244.50
526.0	409	1	409	244.50
553.0	409	1	409	244.50
572.0	410	1	410	243.90
584.0	410	1	410	243.90
Add 0.5 ml. N ₂ H ₄				
	401	1	401	249.38
	402	1	402	248.76
	401	1	401	249.38

PLOT OF THE RATE MEASUREMENT DATA OF
EXPERIMENT NUMBER R35-50
Fig.65

Table 41 Experiment Number R 36-38

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	May 31, 1956
Conductivity cell number	4
Exact bath temperature	-37.9°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	124 mm.
Time spent in wasting chloramine	12 min.
Time spent in collecting chloramine	2.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.93
Volume of chloramine solution transferred to conductivity cell	65 ml.
Time of transferring chloramine solution to conductivity cell	11:20
Time of diluting near the volumetric line with liquid ammonia	11:22
Volume of cell contents at the end of the rate measurement	71.59 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	71.59 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	187.26
Bath below normal operating temperature for 50 min. when immersion knife heater burned out at 76 min. elapsed time. Contents boiled over during final mixing.	

Table 41 Experiment Number R36-38

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
3.0	835	10	8,350	11.98
4.0	740	10	7,400	13.51
4.8	690	10	6,900	14.49
6.0	627	10	6,270	15.95
7.0	573	10	5,730	17.45
8.4	518	10	5,180	19.30
9.5	485	10	4,850	20.62
10.3	463	10	4,630	21.60
11.2	440	10	4,400	22.73
12.4	413	10	4,130	24.21
13.6	393	10	3,930	25.44
14.9	374	10	3,740	26.74
16.2	353	10	3,530	28.33
17.7	337	10	3,370	29.67
18.8	323	10	3,230	30.96
20.3	307	10	3,070	32.57
22.0	293	10	2,930	34.13
24.0	277	10	2,770	36.10
26.1	263	10	2,630	38.02
27.7	253	10	2,530	39.52
30.2	242	10	2,420	41.32
32.6	230	10	2,300	43.48
34.7	220	10	2,200	45.45
37.0	212	10	2,120	47.17
39.3	182	10	1,820	54.94
40.9	1490	1	1,490	67.11
41.3	1410	1	1,410	70.92
41.7	1350	1	1,350	74.07
42.3	1295	1	1,295	77.22
42.7	1235	1	1,235	80.97
43.3	1178	1	1,178	84.89
43.9	1130	1	1,130	88.50
44.7	1080	1	1,080	92.59
45.8	1033	1	1,033	96.80
46.8	1000	1	1,000	100.00
48.0	965	1	965	103.63
49.8	935	1	935	106.95
52.0	905	1	905	110.50

Table 41 Experiment Number R36-38 (cont.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
53.8	883	1	883	113.25
56.9	855	1	855	116.96
60.1	830	1	830	120.48
63.0	810	1	810	123.46
65.0	801	1	801	124.84
67.3	790	1	790	126.58
70.2	778	1	778	128.53
75.8	750	1	750	133.33
123.7	705	1	705	141.84
131.3	701	1	701	142.65
136.0	700	1	700	142.86
Add 0.5 ml. N ₂ H ₄				
	537	1	537	186.22
	540	1	540	185.19
	535	1	535	186.92
	535	1	535	186.92
	533	1	533	187.62
	535	1	535	186.92

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT
NUMBER R36-38

Fig. 66

Table 42 Experiment Number R 37-38

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of measurement	June 2, 1956
Conductivity cell number	4
Exact bath temperature	-37.9°C.
Difference in height of the two limbs of the chlorine manometer expressed in mm. sulfuric acid	128 mm.
Time spent in wasting chloramine	13 min.
Time spent in collecting chloramine	2.25 min.
Fraction of chloramine solution transferred to conductivity cell	0.93
Volume of chloramine solution transferred to conductivity cell	65 ml.
Time of transferring chloramine solution to conductivity cell	11:15
Time of diluting near the volumetric line with liquid ammonia	11:16
Volume of cell contents at the end of the rate measurement	71.59 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	71.59 ml.
Final conductivity reading in reciprocal ohms $\times 10^5$ after adding hydrazine and mixing	213.68
Cell contents boiled over during final mixing	

Table 42 Experiment Number R37⁻³⁸

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal Resistance mhos x 10 ⁵
1.5	840	10	8400	11.90
3.0	700	10	7000	14.28
4.2	615	10	6150	16.26
5.3	555	10	5550	18.02
6.5	507	10	5070	19.72
8.0	455	10	4550	21.98
9.2	423	10	4230	23.64
10.5	393	10	3930	25.44
11.3	374	10	3740	26.74
12.7	354	10	3540	28.25
14.3	331	10	3310	30.21
15.8	314	10	3140	31.85
17.2	297	10	2970	33.67
19.3	278	10	2780	35.97
22.3	257	10	2570	38.91
24.0	247	10	2470	40.48
25.3	233	10	2330	42.92
27.0	228	10	2280	43.86
28.7	219	10	2190	45.66
30.2	212	10	2120	47.17
32.2	203	10	2030	49.26
34.0	198	10	1980	50.50
35.5	1910	1	1910	52.36
37.0	1865	1	1865	53.62
38.3	1815	1	1815	55.09
40.2	1770	1	1770	56.50
42.5	1715	1	1715	58.31
44.2	1670	1	1670	59.88
47.2	1615	1	1615	61.92
49.3	1565	1	1565	63.90
51.5	1525	1	1525	65.57
53.5	1490	1	1490	67.11
55.3	1465	1	1465	68.26
57.8	1422	1	1422	70.32
59.8	1395	1	1395	71.68
61.3	1365	1	1365	73.26
62.0	1345	1	1345	74.35
65.5	1315	1	1315	76.04
67.3	1287	1	1287	77.70
68.5	1205	1	1205	82.99
70.0	865	1	865	115.61
70.2	810	1	810	123.46

Table 42 Experiment Number R37-38 (con't.)

Elapsed time in min. meas- ured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
70.7	775	1	775	129.03
71.0	733	1	733	136.42
71.7	688	1	688	145.35
72.3	662	1	662	151.06
73.0	645	1	645	155.04
74.2	625	1	625	160.00
75.5	610	1	610	163.93
76.8	603	1	603	165.84
78.5	603	1	603	165.84
79.8	598	1	598	167.22
82.3	587	1	587	170.36
84.9	580	1	580	172.41
87.2	575	1	575	173.91
89.5	573	1	573	174.52
93.5	568	1	568	176.06
104.5	565	1	565	176.99
115.8	560	1	560	178.57
142.3	525	1	525	190.48
148.8	522	1	522	191.57
163.0	519	1	519	192.68
175.7	513	1	513	194.94
202.5	507	1	507	197.24
215.2	505	1	505	198.02
230.0	505	1	505	198.02
259.5	501	1	501	199.61
281.7	501	1	501	199.61
314.0	500	1	500	200.00
344.0	499	1	499	200.40
346.3	500	1	500	200.00
350.3	500	1	500	200.00
add 0.50 ml. N ₂ H ₄				
	468	1	468	213.68
	468	1	468	213.68
	468	1	468	213.68
	467	1	467	214.13

Fig. 67

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT NUMBER R37-38

Table 43 Experiment Number R 38-38

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	June 5, 1956
Conductivity cell number	4
Exact bath temperature	-37.9°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	13 min.
Time spent in collecting chloramine	2.0 min.
Fraction of chloramine solution transferred to conductivity cell	0.86
Volume of chloramine solution transferred to conductivity cell	60 ml.
Time of transferring chloramine solution to conductivity cell	2:55
Time of diluting near the volumetric line with liquid ammonia	2:58
Volume of cell contents at the end of the rate measurement	71.09 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.6 ml.
Volume of cell contents after adding hydrazine and mixing	71.34 ml.
Final conductivity reading in reciprocal ohms x 10^5 after adding hydrazine and mixing	180.18

Table 43 Experiment Number R38-38

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
1.7	700	10	7000	14.28
2.3	660	10	6600	15.15
3.7	593	10	5930	16.86
5.2	535	10	5350	18.69
6.8	487	10	4870	20.53
7.9	460	10	4600	21.74
9.5	425	10	4250	23.53
10.8	403	10	4030	24.81
12.2	378	10	3780	26.46
13.7	357	10	3570	28.01
15.2	339	10	3390	29.50
16.8	320	10	3200	31.25
18.7	305	10	3050	32.79
20.0	283	10	2830	35.34
22.7	273	10	2730	36.63
24.4	262	10	2620	38.17
26.2	251	10	2510	39.84
28.2	240	10	2400	41.67
29.7	233	10	2330	42.92
31.6	227	10	2270	44.05
33.7	217	10	2170	46.08
35.3	212	10	2120	47.17
39.3	199	10	1990	50.25
41.2	1950	1	1950	51.28
43.0	1895	1	1895	52.77
44.9	1850	1	1850	54.05
46.9	1800	1	1800	55.56
48.9	1760	1	1760	56.82
50.9	1720	1	1720	58.14
52.6	1680	1	1680	59.52
54.3	1660	1	1660	60.24
57.2	1605	1	1605	62.30
59.8	1570	1	1570	63.69
61.5	1545	1	1545	64.72
63.5	1515	1	1515	66.01
65.7	1490	1	1490	67.11
67.7	1465	1	1465	68.26
70.0	1435	1	1435	69.69
72.0	1405	1	1405	71.17
74.8	1383	1	1383	72.31
78.3	1345	1	1345	74.35

Table 43 Experiment Number R38-38 (con't.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
81.2	1315	1	1315	76.04
84.3	1285	1	1285	77.02
86.7	1265	1	1265	79.05
90.8	1230	1	1230	81.30
95.0	1202	1	1202	83.19
101.0	1163	1	1163	85.98
103.8	885	1	885	112.99
104.0	805	1	805	124.27
104.5	755	1	755	132.45
104.9	705	1	705	141.84
105.2	680	1	680	147.06
105.8	658	1	658	151.98
106.3	627	1	627	159.48
107.2	610	1	610	163.93
108.3	593	1	593	168.63
109.5	583	1	583	171.53
110.7	579	1	579	172.71
113.3				
116.5	573	1	573	174.52
123.5	573	1	573	174.52
134.0	573	1	573	174.52
145.5	573	1	573	174.52
193.0	573	1	573	174.52
209.0	573	1	573	174.52
227.0	572	1	572	174.82
266.0	573	1	573	174.52
300.0	570	1	570	175.44
324.0	573	1	573	174.52
328.0	573	1	573	174.52
add 0.60 ml. N ₂ H ₄				
	555	1	555	180.18
	555	1	555	180.18
	555	1	555	180.18

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT
NUMBER R 38-38 Fig. 68

Table 44 Experiment Number R 39⁻³⁸

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of measurement	June 7, 1956
Conductivity cell number	4
Exact bath temperature	-37.9°C.
Difference in height of the two limbs of the chlorine manometer expressed in mm. sulfuric acid	120 mm.
Time spent in wasting chloramine	14 min.
Time spent in collecting chloramine	2.75 min.
Fraction of chloramine solution transferred to conductivity cell	0.87
Volume of chloramine solution transferred to conductivity cell	65 ml.
Time of transferring chloramine solution to conductivity cell	12:17
Time of diluting near the volumetric line with liquid ammonia	12:19
Volume of cell contents at the end of the rate measurement	72.09 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	72.19 ml.
Final conductivity reading in reciprocal ohms $\times 10^5$ after adding hydrazine and mixing	185.18
The column headed "Concentration of NH_4Cl , moles/liter $\times 10^5$ " was obtained using the equation - conc. of NH_4Cl , moles/liter $\times 10^5$ - antilog $(\frac{1}{a} \log \text{reciprocal resistance} - \frac{b}{a})$ where $(\frac{1}{a}) = 1.3504$ and $(-\frac{b}{a}) = 1.9806$.	

Table 44 Experiment Number R39⁻³⁸

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity bridge dial multi- read- plying ing factor	Resis- tance ohms	Recip- rocal resis- tance mhosx10 ⁵	Conc. NH ₄ Cl moles/liter x 10 ⁵
1.5	873	10	8730	11.45
2.2	798	10	7980	12.53
3.5	710	10	7100	14.08
4.4	655	10	6550	15.27
5.6	595	10	5950	16.81
6.7	543	10	5430	18.42
8.2	483	10	4830	20.70
10.0	443	10	4430	22.57
11.3	412	10	4120	24.27
13.4	375	10	3750	26.67
16.2	336	10	3360	29.76
18.8	311	10	3110	32.15
21.5	288	10	2880	34.72
22.9	277	10	2770	36.10
25.0	262	10	2620	38.17
26.6	253	10	2530	39.52
28.2	244	10	2440	40.98
30.1	237	10	2370	42.19
34.3	214	10	2140	46.73
42.5	1820	1	1820	54.94
44.5	1765	1	1765	56.66
46.0	1715	1	1715	58.31
49.5	1655	1	1655	60.42
51.7	1610	1	1610	62.11
53.5	1575	1	1575	63.49
55.5	1535	1	1535	65.15
60.2	1487	1	1487	67.25
61.5	1457	1	1457	68.63
64.2	1420	1	1420	70.42
67.0	1382	1	1382	72.36
68.5	1367	1	1367	73.15
70.2	1347	1	1347	74.24
72.0	1330	1	1330	75.19
74.5	1305	1	1305	76.63
76.7	1282	1	1282	78.00
82.7	1228	1	1228	81.43
89.0	1182	1	1182	84.60
92.5	1155	1	1155	86.58
95.2	1140	1	1140	87.72

Table 44 Experiment Number R39⁻³⁸ (con't.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity bridge dial read- ing	multi- plying factor	Resis- tance ohms	Recip- rocal resis- tance mhosx10 ⁵	Conc. NH ₄ Cl moles/liter x 10 ⁵
96.7	1135	1	1135	88.10	700.0
99.5	1110	1	1110	90.09	721.4
101.3	1103	1	1103	90.66	727.6
104.0	1082	1	1082	92.42	746.8
106.8	1065	1	1065	93.90	762.5
109.6	1054	1	1054	94.88	773.8
114.3	1021	1	1021	97.94	826.2
119.5	1003	1	1003	99.70	846.4
120.5	1001	1	1001	99.90	850.9
123.8	965	1	965	103.63	891.9
124.3	925	1	925	108.11	944.3
124.7	877	1	877	114.02	1001.3
125.5	820	1	820	121.95	1111.2
126.5	733	1	733	136.42	1293.0
127.0	682	1	682	146.63	1425.0
128.0	633	1	633	157.90	1576.0
128.6	603	1	603	165.84	1683.1
129.3	585	1	585	170.94	1752.7
130.5	567	1	567	176.37	1829.0
131.7	555	1	555	180.18	1882.4
132.8	553	1	553	180.83	1894.5
134.8	555	1	555	180.18	1882.4
140.5	555	1	555	180.18	1882.4
146.7	552	1	552	181.16	1896.3
154.7	548	1	548	182.48	1924.6
166.8	550	1	550	181.82	1909.9
168.5	548	1	548	182.48	1924.7
176.5	552	1	552	181.16	1896.3
202.5	550	1	550	181.82	1909.9
219.5	550	1	550	181.82	1909.9
add 0.5 ml. N ₂ H ₄					
	542	1	542	184.50	1943.6
	540	1	540	185.18	1953.5
	539	1	539	185.53	1958.4

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PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT
NUMBER R39-38 Fig. 69

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT
NUMBER R39-38

Fig. 70

Table 45 Experiment Number R 40⁻³⁸

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	June 9, 1956
Conductivity cell number	4
Exact bath temperature	-37.9°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	130 mm.
Time spent in wasting chloramine	20 min.
Time spent in collecting chloramine	2.5 min.
Fraction of chloramine solution transferred to conductivity cell	0.89
Volume of chloramine solution transferred to conductivity cell	67 ml.
Time of transferring chloramine solution to conductivity cell	1:17
Time of diluting near the volumetric line with liquid ammonia	1:18
Volume of cell contents at the end of the rate measurement	72.09 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	72.09 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	254.45

Table 45 Experiment Number R40⁻³⁸

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
0.5	635	10	6350	15.75
2.0	582	10	5820	17.18
2.8	540	10	5400	18.52
3.7	488	10	4880	20.49
4.7	447	10	4470	22.37
5.3	417	10	4170	23.98
6.5	388	10	3880	25.77
7.7	360	10	3600	27.78
8.8	329	10	3290	30.40
10.0	308	10	3080	32.47
11.2	292	10	2920	34.25
12.6	273	10	2730	36.63
14.1	257	10	2570	38.91
16.1	242	10	2420	41.32
17.9	229	10	2290	43.67
21.2	208	10	2080	48.08
22.5	2000	1	2000	50.00
24.3	1900	1	1900	52.63
26.3	1820	1	1820	54.94
29.2	1705	1	1705	58.65
30.2	1777	1	1777	56.24
32.2	1625	1	1625	61.54
34.2	1570	1	1570	63.69
35.9	1525	1	1525	65.57
37.2	1487	1	1487	67.25
39.5	1440	1	1440	69.44
40.3	1423	1	1423	70.27
42.0	1382	1	1382	72.36
44.8	1335	1	1335	74.91
46.6	1307	1	1307	76.51
50.1	1253	1	1253	79.81
51.8	1222	1	1222	81.83
54.0	1195	1	1195	83.68
57.0	1155	1	1155	86.58
61.2	1105	1	1105	90.50
63.3	1081	1	1081	92.51
65.7	1058	1	1058	94.52
67.2	1042	1	1042	95.97
69.8	1018	1	1018	98.23
71.8	1000	1	1000	100.00
74.1	982	1	982	101.83
77.0	960	1	960	104.17
78.3	927	1	927	107.87

Table 45 Experiment Number R40-38 (con't.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal Resistance mhos x 10 ⁵
79.0	895	1	895	111.73
79.4	873	1	873	114.55
80.0	850	1	850	117.65
80.3	832	1	832	120.19
80.8	798	1	798	125.31
81.8	755	1	755	132.45
82.3	733	1	733	136.42
82.8	705	1	705	141.84
83.3	688	1	688	145.35
84.0	658	1	658	151.98
85.0	625	1	625	160.00
85.4	605	1	605	165.29
86.1	598	1	598	167.22
86.8	582	1	582	171.82
87.8	554	1	554	180.50
88.3	545	1	545	183.49
88.9	535	1	535	186.92
89.5	523	1	523	191.20
90.4	508	1	508	196.85
91.8	493	1	493	202.84
92.8	483	1	483	207.04
93.8	476	1	476	210.08
94.9	467	1	467	214.13
96.5	457	1	457	218.82
99.5	444	1	444	225.22
101.0	442	1	442	226.24
103.2	433	1	433	230.95
106.0	427	1	427	234.19
107.7	427	1	427	234.19
116.3	418	1	418	239.23
122.0	417	1	417	239.81
149.0	410	1	410	243.90
160.5	413	1	413	242.13
170.7	408	1	408	245.10
177.3	409	1	409	244.50
187.0	407	1	407	245.70
204.5	407	1	407	245.70
227.0	407	1	407	245.70
add 0.5 ml. N ₂ H ₄				
	397	1	397	251.89
	392	1	392	255.10
	393	1	393	254.45

Fig. 71

PLOT OF THE RATE MEASUREMENT DATA OF
EXPERIMENT NUMBER R 40-38

Table 46 Experiment Number R 41-38

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	June 19, 1956
Conductivity Cell number	5
Exact bath temperature	-37.9°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	14 min.
Time spent in collecting chloramine	2 min.
Fraction of chloramine solution transferred to conductivity cell	0.87
Volume of chloramine solution transferred to conductivity cell	65 ml.
Time of transferring chloramine solution to conductivity cell	3:04
Time of diluting near the volumetric line with liquid ammonia	3:05
Volume of cell contents at the end of the rate measurement	73.10 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	73.60 ml.
Final conductivity reading in reciprocal ohms x 10^5 after adding hydrazine and mixing	307.69

Table 46 Experiment Number R41-38

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
1.7	230	10	2300	43.48
3.8	287	10	2370	42.19
5.0	218	10	2180	45.87
9.0	215	10	2150	46.51
11.0	200	10	2000	50.00
16.5	165	10	1650	60.61
20.0	150	10	1500	66.67
22.0	140	10	1400	71.43
25.0	130	10	1300	76.92
30.0	120	10	1200	83.33
35.0	1075	1	1075	93.02
40.0	995	1	995	100.50
45.0	927.5	1	927.5	107.82
49.0	880	1	880	113.64
55.0	830	1	830	120.48
64.0	765	1	765	130.72
71.0	715	1	715	139.86
76.0	610	1	610	163.93
80.0	530	1	530	188.68
85.0	470	1	740	212.76
91.0	425	1	425	235.29
95.0	395	1	395	253.16
100.0	385	1	385	259.74
101.0	360	1	360	277.78
119.0	350	1	350	285.71
123.0	335	1	335	298.51
135.0	325	1	325	307.69
174.0	325	1	325	307.69
186.0	325	1	325	307.69
add 0.5 ml. N ₂ H ₄				
	325	1	325	307.69

PLOT OF THE RATE MEASUREMENT DATA OF EXPERIMENT
NUMBER R41-38

Fig. 72

Table 47 Experiment Number R 42⁻³⁸

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	June 21, 1956
Conductivity cell number	5
Exact bath temperature	-37.9°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	136 mm.
Time spent in wasting chloramine	15 min.
Time spent in collecting chloramine	2 min.
Fraction of chloramine solution transferred to conductivity cell	0.93
Volume of chloramine solution transferred to conductivity cell	65 ml.
Time of transferring chloramine solution to conductivity cell	11:52
Time of diluting near the volumetric line with liquid ammonia	11:53
Volume of cell contents at the end of the rate measurement	73.10 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	73.60 ml.
Final conductivity reading in reciprocal ohms x 10 ³ after adding hydrazine and mixing	389.10

Table 47 Experiment Number R42⁻³⁸

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial. reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ³
2.0	250	10	2500	40.00
3.5	230	10	2300	43.48
5.0	210	10	2100	47.62
6.5	189	10	1890	52.91
8.0	180	10	1800	55.56
10.0	163	10	1630	61.35
12.0	152	10	1520	65.79
13.0	141	10	1410	70.92
15.5	1265	1	1265	79.05
18.0	1205	1	1205	82.99
22.0	1045	1	1045	95.69
24.2	102	10	1020	98.04
27.0	930	1	930	107.53
30.7	860	1	860	116.28
33.0	840	1	840	119.05
34.5	825	1	825	121.21
37.0	790	1	790	126.6
40.0	760	1	760	131.58
44.0	720	1	720	138.89
46.0	703	1	703	142.25
48.0	697	1	697	143.47
50.5	660	1	660	151.52
53.5	645	1	645	155.04
58.5	605	1	605	165.29
62.5	573	1	573	174.52
67.0	533	1	533	187.62
70.3	505	1	505	198.02
74.0	388	1	388	257.73
75.0	363	1	363	275.48
76.0	338	1	338	295.86
77.5	316	1	316	316.46
79.2	293	1	293	341.30
81.5	285	1	285	350.88
83.5	278	1	278	359.71
87.0	268	1	268	373.13
89.0	265	1	265	377.36
91.0	265	1	265	377.36
94.0	265	1	265	377.36
98.0	265	1	265	377.36

Table 47 Experiment Number R42-38 (con't.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
105.5	265	1	265	377.36
115.0	263	1	263	380.23
128.0	258	1	258	387.60
138.0	258	1	258	387.60
149.0	258	1	258	387.60
153.0	258	1	258	387.60
170.0	258	1	258	387.60
197.0	255	1	255	392.16
234.0	258	1	258	387.60
273.0	258	1	258	387.60
add 0.5 ml. N ₂ H ₄				
	258	1	258	387.60
	257	1	257	389.10
	258	1	258	387.60
	255	1	255	392.16

Fig. 73

PLOT OF THE RATE MEASUREMENT DATA
OF EXPERIMENT NUMBER R42-38

Table 48 Experiment Number R 43-38

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	June 23, 1956
Conductivity cell number	5
Exact bath temperature	-37.9°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	128 mm.
Time spent in wasting chloramine	10 min.
Time spent in collecting chloramine	2 min.
Fraction of chloramine solution transferred to conductivity cell	0.87
Volume of chloramine solution transferred to conductivity cell	65 ml.
Time of transferring chloramine solution to conductivity cell	12:12
Time of diluting near the volumetric line with liquid ammonia	12:13
Volume of cell contents at the end of the rate measurement	73.10 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	73.10 ml.
Final conductivity reading in reciprocal ohms $\times 10^5$ after adding hydrazine and mixing	500.00
Bath below normal operating temperature for 3 minutes at 8 minutes elapsed time. Contents boiled over during final mixing.	

Table 48 Experiment Number R43⁻³⁸

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
1.5	410	10	4100	24.39
2.5	390	10	3900	25.64
3.7	384	10	3840	26.04
6.0	370	10	3700	27.03
8.0	370	10	3700	27.03
9.0	340	10	3400	29.41
10.0	318	10	3180	31.45
11.0	265	10	2650	37.74
11.5	248	10	2480	40.32
12.2	232	10	2320	43.10
12.8	218	10	2180	45.87
13.5	204	10	2040	49.02
14.3	1935	1	1935	51.68
15.7	1780	1	1780	56.80
16.3	1710	1	1710	58.48
17.5	1600	1	1600	62.50
18.4	1525	1	1525	65.57
19.5	1460	1	1460	68.49
20.6	1380	1	1380	72.46
22.3	1300	1	1300	76.92
24.0	1215	1	1215	82.30
26.0	1147	1	1147	87.18
29.0	1050	1	1050	95.24
32.5	958	1	958	104.38
34.3	917	1	917	109.05
36.5	878	1	878	113.90
39.3	830	1	830	120.48
40.8	805	1	805	124.22
43.2	774	1	774	129.20
44.8	757	1	757	132.10
49.3	703	1	703	142.25
51.7	677	1	677	147.71
53.7	660	1	660	151.52
57.8	623	1	623	160.51
60.3	605	1	605	165.29
66.0	565	1	565	176.99
69.9	547	1	547	182.82
73.0	533	1	533	187.62
76.3	518	1	518	193.05
78.7	502	1	503	198.81
83.0	488	1	488	204.92
86.8	474	1	474	210.97

Table 48 Experiment Number R43⁻³⁸ (con't.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
93.0	453	1	453	220.75
98.5	433	1	433	230.95
103.4	417	1	417	239.81
108.0	402	1	402	248.76
111.3	390	1	390	256.41
117.7	363	1	363	275.48
121.0	348	1	348	287.36
124.3	333	1	333	300.30
127.0	324	1	324	308.64
130.0	317	1	317	315.46
131.8	310	1	310	322.58
133.8	303	1	303	330.03
138.3	291	1	291	343.64
140.8	288	1	288	347.22
143.7	280	1	280	357.14
147.7	270	1	270	370.37
154.5	262	1	262	381.68
160.4	252	1	252	396.82
163.3	249	1	249	401.61
167.7	242	1	242	413.22
175.2	232	1	232	431.03
183.0	227	1	227	440.53
198.0	215	1	215	465.12
221.5	204	1	204	490.20
243.0	207	1	207	483.10
247.0	204	1	204	490.20
267.0	205	1	205	487.80
277.0	207	1	207	483.09
308.0	208	1	208	480.77
314.0	206	1	206	485.44
add about 1 ml. N ₂ H ₄ , didn't get into vessel				
	200	1	200	500.00

Fig. 74

PLOT OF THE RATE MEASUREMENT
DATA OF EXPERIMENT NUMBER R43-38

Table 49 Experiment Number R 44-38

Rate Measurement Data

Data taken in the measurement of the rate of formation of ammonium chloride from the reaction occurring in a solution composed initially of chloramine dissolved in anhydrous ammonia.

Date of the measurement	June 29, 1956
Conductivity cell number	5
Exact bath temperature	-37.9°C.
Difference in height of the two limbs of the chlorine manometer expressed in millimeters of sulfuric acid	120 mm.
Time spent in wasting chloramine	15 min.
Time spent in collecting chloramine	2 min.
Fraction of chloramine solution transferred to conductivity cell	0.89
Volume of chloramine solution transferred to conductivity cell	71 ml.
Time of transferring chloramine solution to conductivity cell	11:50
Time of diluting near the volumetric line with liquid ammonia	none added
Volume of cell contents at the end of the rate measurement	73.10 ml.
Volume of liquid hydrazine added to the conductivity cell to convert all the unreacted chloramine to ammonium chloride	0.5 ml.
Volume of cell contents after adding hydrazine and mixing	73.10 ml.
Final conductivity reading in reciprocal ohms x 10 ⁵ after adding hydrazine and mixing	454.54

Table 49 Experiment Number R44⁻³⁸

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
3.0	217	10	2170	46.08
3.3	205	10	2050	48.78
3.7	200	10	2000	50.00
4.4	--	--	--	--
6.0	1777	10	1770	56.50
7.2	1665	1	1665	60.06
9.2	1510	1	1510	66.22
10.3	1445	1	1445	69.20
11.7	1355	1	1355	73.80
13.6	1278	1	1278	78.25
15.2	1227	1	1227	81.50
17.3	1135	1	1135	88.10
19.2	1067	1	1067	93.72
22.6	987	1	987	101.32
24.9	937	1	937	106.72
27.2	902	1	902	110.86
28.5	875	1	875	114.28
30.0	838	1	838	119.33
31.7	823	1	823	121.51
33.2	800	1	800	125.00
35.2	763	1	763	131.04
37.3	740	1	740	135.14
39.0	734	1	734	136.24
41.2	707	1	707	141.44
43.8	681	1	681	146.84
47.0	647	1	647	154.56
51.2	623	1	623	160.51
53.7	606	1	606	165.02
55.5	593	1	593	168.63
57.2	575	1	575	173.91
61.0	557	1	557	179.53
63.3	545	1	545	183.49
65.8	535	1	535	186.92
68.8	522	1	522	191.57
72.3	514	1	514	194.55
74.3	505	1	505	198.02
77.3	494	1	494	202.43
81.8	478	1	478	209.20
84.1	470	1	470	212.76
86.8	464	1	464	215.52

Table 49 Experiment Number 44⁻³⁸ (con't.)

Elapsed time in min. mea- sured from the time of the dilution with ammonia	Conductivity dial reading	bridge multi- plying factor	Resistance ohms	Reciprocal resistance mhos x 10 ⁵
89.7	453	1	453	220.75
92.6	443	1	443	225.73
97.0	437	1	437	228.83
102.6	423	1	423	236.41
103.2	414	1	414	241.54
105.7	411	1	411	243.31
111.0	403	1	403	248.14
119.0	392	1	392	255.10
123.3	384	1	384	260.42
125.7	378	1	378	264.55
131.3	373	1	373	268.10
141.2	358	1	358	279.33
146.3	350	1	350	285.71
149.0	338	1	338	295.86
151.5	324	1	324	308.64
154.7	313	1	313	319.49
156.3	303	1	303	330.03
159.0	295	1	295	338.98
160.7	283	1	283	353.36
164.0	278	1	278	359.71
166.8	267	1	267	374.53
169.3	261	1	261	383.14
172.5	253	1	253	395.26
178.0	241	1	241	414.94
184.3	232	1	232	431.03
191.0	228	1	228	438.60
196.7	225	1	225	448.44
210.7	225	1	225	448.44
218.3	223	1	223	448.43
226.7	224	1	224	446.43
249.0	228	1	228	438.60
255.0	227	1	227	440.53
285.0	229	1	229	436.68
296.0	230	1	230	434.78
add 0.5 ml. N ₂ H ₄				
	220	1	220	454.54
	219	1	219	456.62
	220	1	220	454.54
	220	1	220	454.54
	222	1	222	450.45

Fig. 75

PLOT OF THE RATE MEASUREMENT DATA
OF EXPERIMENT NUMBER R44-38

Specific Reaction Rate Constants for the Formation

Reaction

Reaction rate measurement data are described on pages 115-118 . Reference is made there to other parts of this work which apply to the determination of the rate constants.

Derivation of an expression for the specific reaction rate constant for the formation reaction.- It is possible to begin with the empirical relationship between the concentration of ammonium chloride and the reciprocal cell resistance described on pages 98-99 and summarized in equation (16)

$$\log \text{conc.} = \frac{1}{a} \log (\text{recip.resist.}) - \frac{b}{a} \quad (16)$$

and to derive an expression for the specific reaction rate constant for the formation reaction expressed directly in terms of the rate measurement data and of the calibration constants of the conductivity cell.

As explained on pages 99-107 the calculation of concentrations in the reaction mixture depends on a knowledge of the ammonium chloride concentration at any time and of the final corrected ammonium chloride concentration after all the chloramine has been converted to ammonium chloride through reaction either with ammonia or hydrazine.

Equation (16) can be expressed in the antilog form

$$\text{Conc. NH}_4\text{Cl} = 10^{-\frac{b}{a} \text{ recip.resist. } \frac{1}{a}} \quad (25)$$

When the terms A and B replace $\frac{1}{a}$ and $10^{\frac{b}{a}}$, respectively, the equation becomes

$$\text{Conc. NH}_4\text{Cl} = B \text{ recip.resist.}^A \quad (26)$$

The differentiated form of the rate expression was employed in the calculations and slopes taken from large working graphs were used for obtaining numerical values of the derivatives.

Since ammonia is the solvent as well as a reactant in the process, its concentration remains substantially constant, and conditions will only allow observation of the dependence of the rate on the chloramine concentration. This leads to the rate expression

$$-\frac{d \text{ conc. NH}_2\text{Cl}}{dt} = + \frac{d \text{ conc. NH}_4\text{Cl}}{dt} = k \text{ conc. NH}_2\text{Cl}^n \quad (27)$$

The concentration of chloramine at any time is replaced by its equivalent, $C_F - \text{conc. NH}_4\text{Cl}$, or $C_F - B \text{ recip.resist.}^A$. The derivative is expressed as the product of two derivative expressions, the first obtainable in principle from the calibration graph and the second from the rate measurement curve.

The equation becomes

$$\begin{aligned} \frac{d \text{ conc. NH}_2\text{Cl}}{dt} &= + \left(\frac{d \text{ conc. NH}_4\text{Cl}}{d \text{ recip.resist.}} \right) \left(\frac{d \text{ recip.resist.}}{dt} \right) \\ &= k (C_F - B \text{ recip.resist.}^A)^n \end{aligned} \quad (28)$$

The first derivative of the concentration of ammonium chloride with respect to reciprocal cell resistance, obtained from equation (26) is

$$\frac{d \text{ conc. NH}_4\text{Cl}}{d \text{ recip.resist.}} = A B \text{ recip.resist.}^{A-1} \quad (29)$$

Replacement of this value for the derivative in equation (28) leads to

$$\frac{d \text{ recip.resist.}}{dt} = \frac{k (C_F - B \text{ recip.resist.}^A)^n}{A B \text{ recip.resist.}^{A-1}} \quad (30)$$

and

$$\frac{d \text{ recip.resist.}}{dt} = - \frac{\frac{d \text{ conc. NH}_2\text{Cl}}{dt}}{A B \text{ recip.resist.}^{A-1}} \quad (31)$$

Equation (31) is included to emphasize the relationship between the time rate of change of chloramine and the time rate of change of the reciprocal cell resistance.

The expression for the specific reaction rate constant becomes

$$k = \frac{A B \text{ recip.resist.}^{A-1} \left(\frac{d \text{ recip.resist.}}{dt} \right)}{(C_F - B \text{ recip.resist.}^A)^n} \quad (32)$$

Table 50 Rate Constants of the Formation Reaction

Calculation of specific reaction rate constants for the reaction between ammonia and chloramine assuming that the rate has pseudo first order dependence on the chloramine concentration. The following equation applies:

$$K = AB \left(\frac{d \text{ recip.resist.}}{dt} \right) / (C_F - B \text{ recip.resist.}^4)$$

Tabulation of
1/a, -b/a, C_F
for each rate
experiment

Experiment
number and
temperature,
°C.

Point of contact of tangent on curve
Elapsed time,
minutes

Recip. resist.
mhos x 10³

$\frac{d \text{ recip.resist.}}{dt} =$
 $\frac{\text{mhos}_2 - \text{mhos}_1}{t_2 - t_1} \times 10^5$

$10^{-b/a}$
recip.resist.^{1/a}

$C_F - 10^{-b/a}$
recip.resist.^{1/a}

$\frac{10^{-b/a}}{a}$
recip.resist.^{1/a}

$\frac{10^{-b/a} \text{ recip.resist.}^{\frac{1-a}{a}}}{a(C_F - 10^{-b/a} \text{ recip.resist.}^{\frac{1}{a}})^{\frac{1-a}{a}}}$

$K_1 \times 10^5$

1/a = 1.3667
-b/a = 2.3160
C_F = 0.01263

R1-75

375.0

8.83

0.003950

0.00060

0.01203

6.752

561.0

2.216

1/a = 1.3667
-b/a = 2.3160
C_F = 0.01578

R2-75

319.0

7.55

0.005643

0.00048

0.01530

8.713

569.6

3.214

1/a = 1.3667
-b/a = 2.3160
C_F = 0.01639

R3-75

532.0

8.5

0.005552

0.00056

0.01583

9.098

574.8

3.191

1/a = 1.3667
-b/a = 2.3160
C_F = 0.01298

R4-75

210.0

5.80

0.004953

0.00034

0.01264

7.908

625.6

3.099

1,950.0

13.40

0.003857

0.00105

0.01192

10.752

901.8

3.478

3,700.0

19.43

0.003145

0.00175

0.01123

12.322

1,097.6

3.452

5,650.0

24.90

0.002664

0.00246

0.01052

13.495

1,283.0

3.418

1/a = 1.3316
-b/a = 2.0792
C_F = 0.02616

R23-60

50.0

15.60

0.08752

0.00100

0.02516

8.737

347.3

30.394

130.0

22.10

0.07263

0.00163

0.02453

9.807

399.8

29.037

227.5

28.90

0.06874

0.00232

0.02383

10.719

449.8

30.916

375.0

38.85

0.05812

0.00345

0.02271

11.824

520.6

30.360

475.0

44.20

0.04990

0.00409

0.02206

12.341

559.3

27.910

where, as is shown on pages 2295-297 and in Figure 77 the order, "n", with respect to the chloramine concentration is one.

The values of the specific reaction rate constants of the formation reaction.- A summary of calculations leading to the specific reaction rate constants is given in Table 50. The rate constants were calculated for regions of reaction beginning at time zero and ending at the end of the experiment or just before the decomposition reaction began in those cases in which the break occurred.

Experiments R1⁻⁷⁵ through R4⁻⁷⁵ exhibited no break. The rate constants were substantially invariant over the entire course of the reaction measured, a period of 800 to 900 minutes. However, experiment R4⁻⁷⁵ was allowed to proceed under constant supervision for 7,200 minutes until a cake of ice, derived from the moisture of the atmosphere, immobilized all the parts of the bath and terminated the operation. The rate constants were still unchanged throughout this period.

Experiments R5⁻⁷⁵ through R22⁻⁷⁵ usually had relatively short pre-break regions. In most of these cases the formation reaction was in the process of merging with the decomposition reaction and calculations of the formation rate constants were usually not

Table 50 Rate Constants of the Formation Reaction (cont.)

Tabulation of
1/a, -b/a, C_F
for each rate
experiment

Experiment
number and
temperature,
°C.

Point of contact of
tangent on curve
Elapsed time,
minutes

Recip. resist.
mhos x 10⁵

$\frac{d \text{ recip. resist. }}{dt}$
 $\frac{mhos_2 - mhos_1}{t_2 - t_1} \times 10^5$

1/a = 1.3316 -b/a = 2.0792 C _F = 0.02345	R24-60	25.0	11.9	0.08587
		87.5	16.7	0.07389
		187.5	23.3	0.06456
		325.0	31.55	0.05790
1/a = 1.3316 -b/a = 2.0792 C _F = 0.02828	R25-60	80.0	21.20	0.07752
		275.0	35.30	0.06600
		335.0	38.80	0.06100
		525.0	49.80	0.05644
		575.0	52.95	0.05364
1/a = 1.3316 -b/a = 2.0792 C _F = 0.02964	R26-60	47.5	20.70	0.08012
		135.0	27.40	0.06968
		265.0	35.80	0.06000
		410.0	44.20	0.05587
		627.5	56.10	0.05345
		727.5	61.20	0.04954
		827.5	65.60	0.04524

$10^{-b/a}$
recip. resist. $\frac{1}{a}$

$C_F \cdot 10^{-b/a}$
recip. resist. $\frac{1}{a}$

$\frac{10^{-b/a}}{a}$
recip. resist. $\frac{1-a}{a}$

$\frac{10^{-b/a} \text{ recip. resist. } \frac{1-a}{a}}{a(C_F \cdot 10^{-b/a} \text{ recip. resist. } \frac{1-a}{a})} \frac{1}{a}$

$K_1 \times 10^5$

0.00071	0.02274	7.988	351.3	30.166
0.00112	0.02233	8.938	400.2	29.573
0.00174	0.02171	9.981	459.8	29.684
0.00261	0.02084	11.037	529.6	30.666
0.00154	0.02674	9.673	361.7	28.038
0.00304	0.02525	11.454	453.6	29.940
0.00344	0.02484	11.821	475.9	29.028
0.00480	0.02348	12.840	546.8	30.859
0.00521	0.02308	13.103	567.8	30.457
0.00149	0.02814	9.599	341.0	27.325
0.00217	0.02747	10.534	383.5	26.722
0.00309	0.02654	11.511	433.7	26.021
0.00409	0.02554	12.343	483.2	26.999
0.00563	0.02401	13.366	556.7	29.756
0.00631	0.02332	13.750	589.5	29.204
0.00693	0.02271	14.071	619.6	28.033

Table 50 Rate Constants of the Formation Reaction (cont.)

Tabulation of $1/a$, $-b/a$, C_F for each rate experiment	Experiment number and temperature, °C.	Point of contact of tangent on curve Elapsed time, minutes	Recip. resist. mhos $\times 10^5$	$\frac{d \text{ recip. resist. }}{dt} =$ $\frac{mhos_2 - mhos_1}{t_2 - t_1} \times 10^5$
$1/a = 1.3316$ $-b/a = 2.0792$ $C_F = 0.02962$	R27-60	50.0	17.30	0.09432
		105.0	21.70	0.08179
		380.0	40.75	0.06044
		612.5	53.55	0.05300
		800.0	63.00	0.04556
$1/a = 1.3316$ $-b/a = 2.0792$ $C_F = 0.01983$	R28-60	37.5	8.75	0.07137
		92.5	13.50	0.06273
		262.5	23.30	0.05195
		537.5	35.85	0.04130
		675.0	41.45	0.03552
$1/a = 1.3432$ $-b/a = 2.0531$ $C_F = 0.02708$	R29-50	20.0	21.27	0.3227
		95.0	41.25	0.2491
		155.0	55.25	0.2079
		262.5	74.90	0.1580
		387.5	93.60	0.1212
		562.5	114.10	0.1119
		600.0	118.05	0.1038

$10^{-b/a}$ recip. resist. $1/a$	$C_F - 10^{-b/a}$ recip. resist. $1/a$	$\frac{10^{-b/a}}{a}$ recip. resist. $\frac{1-a}{a}$	$\frac{10^{-b/a} \text{ recip. resist. } \frac{1-a}{a}}{a(C_F - 10^{-b/a} \text{ recip. resist. } \frac{1-a}{a})}$	$K_1 \times 10^5$
0.00117	0.02845	9.043	317.9	29.983
0.00160	0.02802	9.764	348.4	28.497
0.00367	0.02595	12.015	463.0	27.986
0.00529	0.02433	13.156	540.6	28.653
0.00656	0.02306	13.884	602.2	27.434
0.00047	0.01936	7.214	372.7	26.603
0.00084	0.01898	8.329	438.7	27.522
0.00174	0.01808	9.982	552.0	28.676
0.00310	0.01673	11.516	688.4	28.429
0.00376	0.01607	12.084	752.0	26.709
0.00132	0.02576	8.339	323.8	104.48
0.00321	0.02386	10.467	438.6	109.26
0.00476	0.02232	11.572	518.5	107.80
0.00716	0.01992	12.845	644.9	101.90
0.00966	0.01742	13.868	796.2	96.50
0.01260	0.01447	14.843	1,025.6	114.76
0.01319	0.01388	15.015	1,081.4	112.25

Table 50 Rate Constants of the Formation Reaction (cont.)

Tabulation of
1/a, -b/a, C_F
for each rate
experiment

Experiment
number and
temperature
°C.

Point of contact of tangent on curve
Elapsed time,
minutes

Recip. resist.
mhos x 10⁵

$\frac{d \text{ recip. resist. }}{dt} = \frac{mhos_2 - mhos_1}{t_2 - t_1} \times 10^5$

$10^{-b/a}$
recip. resist. $1/a$

$C_F - 10^{-b/a}$
recip. resist. $1/a$

$\frac{10^{-b/a}}{a}$
recip. resist. $\frac{1-a}{a}$

$\frac{10^{-b/a} \text{ recip. resist. } \frac{1-a}{a}}{a(C_F - 10^{-b/a} \text{ recip. resist. } \frac{1}{a})}$

$K_1 \times 10^5$

1/a = 1.3432
-b/a = 2.0531
C_F = 0.02784

R30-50

Elapsed time, minutes	Recip. resist. mhos x 10 ⁵	$\frac{d \text{ recip. resist. }}{dt} \times 10^5$
12.5	15.60	0.3760
32.5	22.60	0.3452
70.0	33.90	0.2760
100.0	41.80	0.2560

$10^{-b/a}$ recip. resist. $1/a$	$C_F - 10^{-b/a}$ recip. resist. $1/a$	$\frac{10^{-b/a}}{a}$ recip. resist. $\frac{1-a}{a}$	$\frac{10^{-b/a} \text{ recip. resist. } \frac{1-a}{a}}{a(C_F - 10^{-b/a} \text{ recip. resist. } \frac{1}{a})}$	$K_1 \times 10^5$
0.00087	0.02697	7.498	278.0	104.52
0.00143	0.02641	8.514	322.4	111.28
0.00247	0.02537	9.786	385.7	106.45
0.00327	0.02457	10.498	427.2	109.37

1/a = 1.3432
-b/a = 2.0531
C_F = 0.02378

R31-50

Elapsed time, minutes	Recip. resist. mhos x 10 ⁵	$\frac{d \text{ recip. resist. }}{dt} \times 10^5$
15.0	15.50	0.2994
52.5	26.10	0.2558
98.5	37.00	0.2142
152.5	47.50	0.1865
200.0	56.00	0.1640
256.0	65.00	0.1778
295.0	70.90	0.1490

$10^{-b/a}$ recip. resist. $1/a$	$C_F - 10^{-b/a}$ recip. resist. $1/a$	$\frac{10^{-b/a}}{a}$ recip. resist. $\frac{1-a}{a}$	$\frac{10^{-b/a} \text{ recip. resist. } \frac{1-a}{a}}{a(C_F - 10^{-b/a} \text{ recip. resist. } \frac{1}{a})}$	$K_1 \times 10^5$
0.00086	0.02292	7.480	326.4	97.73
0.00174	0.02204	8.946	405.8	103.82
0.00278	0.02100	10.084	480.1	102.84
0.00388	0.01990	10.986	552.1	102.98
0.00484	0.01893	11.626	614.0	100.70
0.00592	0.01786	12.236	685.0	121.80
0.00665	0.01713	12.607	736.1	109.67

1/a = 1.3432
-b/a = 2.0531
C_F = 0.02325

R32-50

Elapsed time, minutes	Recip. resist. mhos x 10 ⁵	$\frac{d \text{ recip. resist. }}{dt} \times 10^5$
7.5	14.20	0.3276
22.5	18.15	0.2964
47.5	25.20	0.2576
80.0	33.10	0.2267
135.0	44.30	0.1865
212.5	57.85	0.1669
270.0	67.00	0.1543

$10^{-b/a}$ recip. resist. $1/a$	$C_F - 10^{-b/a}$ recip. resist. $1/a$	$\frac{10^{-b/a}}{a}$ recip. resist. $\frac{1-a}{a}$	$\frac{10^{-b/a} \text{ recip. resist. } \frac{1-a}{a}}{a(C_F - 10^{-b/a} \text{ recip. resist. } \frac{1}{a})}$	$K_1 \times 10^5$
0.00077	0.02254	7.260	322.0	105.51
0.00107	0.02218	7.927	357.3	105.92
0.00166	0.02159	8.839	409.4	105.44
0.00245	0.02080	9.706	466.5	105.76
0.00354	0.01971	10.726	544.1	101.47
0.00506	0.01819	11.755	646.3	107.87
0.00616	0.01708	12.363	723.7	111.66

Table 50 Rate Constants of the Formation Reaction (cont.)

Tabulation of 1/a, -b/a, C _F for each rate experi- ment	Experiment number and temperature, °C.	Point of contact of tangent on curve Elapsed time, minutes	Recip. resist. mhos x 10 ⁵	$\frac{d \text{ recip.resist.}}{dt} = \frac{\text{mhos}_2 - \text{mhos}_1}{t_2 - t_1} \times 10^5$	$10^{-b/a}$ recip.resist., 1/a	C _F -10 ^{-b/a} recip.resist., 1/a	$\frac{10^{-b/a}}{a}$ recip.resist., $\frac{1-a}{a}$	$\frac{10^{-b/a} \text{ recip.resist. } \frac{1-a}{a}}{a(C_F - 10^{-b/a} \text{ recip.resist. } \frac{1-a}{a})} \times 1/a$	K ₁ x 10 ⁵
1/a = 1.3432 -b/a = 2.0531 C _F = 0.02171	R33-50	10.0	12.00	0.3204	0.00061	0.02110	6.852	324.8	104.07
		27.5	17.37	0.2783	0.00100	0.02070	7.779	375.8	104.58
		65.0	26.50	0.2345	0.00177	0.01993	8.993	451.2	105.80
		105.0	35.10	0.2045	0.00259	0.01912	9.891	517.3	105.79
		180.0	48.30	0.1636	0.00397	0.01774	11.049	623.0	101.92
		277.5	64.00	0.1448	0.00580	0.01591	12.171	765.0	110.77
		382.5	77.00	0.1132	0.00743	0.01428	12.966	908.2	102.81
		525.0	91.50	0.09476	0.00937	0.01234	13.760	1,115.3	105.69
		705.0	106.65	0.07665	0.01152	0.01019	14.502	1,422.9	109.06
1/a = 1.3432 -b/a = 2.0531 C _F = 0.029867	R34-50	5.0	17.80	0.3725	0.00104	0.02883	7.846	272.2	101.38
		37.5	28.80	0.3140	0.00198	0.02788	9.254	331.9	104.21
		75.0	39.15	0.2677	0.00300	0.02687	10.281	382.6	102.42
1/a = 1.3432 -b/a = 2.0531 C _F = 0.03598	R35-50	12.5	23.20	0.4215	0.00148	0.03449	8.590	249.0	104.98
		60.0	39.90	0.3350	0.00307	0.03290	10.350	314.6	105.38
		82.5	47.20	0.3170	0.00385	0.03212	10.963	341.2	108.13
		142.5	64.30	0.2655	0.00583	0.03014	12.190	404.4	107.38
		255.0	90.30	0.2150	0.00920	0.02677	13.697	511.6	110.00
		337.5	106.30	0.1838	0.01146	0.02452	14.485	590.8	108.59

Table 50 Rate Constants of the Formation Reaction (cont.)

Tabulation of $1/a$, $-b/a$, C_F for each rate experiment	Experiment number and temperature, $^{\circ}C$.	Point of contact of tangent on curve Elapsed time, minutes	Recip. resist. mhos $\times 10^5$	$\frac{d \text{ recip. resist.}}{dt}$ $\frac{\text{mhos}_2 - \text{mhos}_1}{t_2 - t_1} \times 10^5$	$10^{-b/a}$ recip. resist. $1/a$	$C_F - 10^{-b/a}$ recip. resist. $1/a$	$\frac{10^{-b/a}}{a}$ recip. resist. $\frac{1-a}{a}$	$\frac{10^{-b/a} \text{ recip. resist. } \frac{1-a}{a}}{a(C_F - 10^{-b/a} \text{ recip. resist. } \frac{1}{a})}$	$K_1 \times 10^5$
$1/a = 1.3504$ $-b/a = 1.9806$ $C_F = 0.01987$	R36-38	6.7	17.00	1.4115	0.00078	0.01909	6.170	323.2	456.18
		25.0	36.70	0.9640	0.00220	0.01767	8.079	457.2	440.74
		33.5	44.50	0.8360	0.00285	0.01702	8.643	507.8	424.56
$1/a = 1.3504$ $-b/a = 1.9806$ $C_F = 0.02370$	R37-38	3.0	14.00	1.9318	0.00060	0.02310	5.763	249.5	481.96
		5.0	18.50	1.7917	0.00087	0.02283	6.354	278.4	498.74
		17.8	34.00	1.1623	0.00198	0.02171	7.864	362.2	420.98
		36.5	53.00	0.9119	0.00361	0.02009	9.189	457.4	417.09
		55.0	68.00	0.7943	0.00505	0.01865	10.027	537.7	427.09
$1/a = 1.3504$ $-b/a = 1.9806$ $C_F = 0.01889$	R38-38	9.0	23.50	1.1469	0.00120	0.01769	6.910	390.7	448.06
		18.0	32.50	0.9994	0.00186	0.01703	7.742	454.7	454.45
		26.0	39.50	0.8490	0.00242	0.01646	8.290	503.6	427.52
		55.0	60.75	0.6516	0.00434	0.01455	9.640	662.4	431.61
		73.0	71.50	0.5623	0.00540	0.01348	10.206	756.9	425.58
		93.0	82.25	0.5068	0.00653	0.01236	10.719	867.2	439.49
$1/a = 1.3504$ $-b/a = 1.9806$ $C_F = 0.01956$	R39-38	5.0	15.50	1.4367	0.00068	0.01888	5.973	316.4	454.59
		17.5	31.00	1.0500	0.00175	0.01781	7.615	427.5	448.87
		31.0	43.50	0.9404	0.00276	0.01680	8.574	510.4	479.95
		53.0	63.00	0.7281	0.00455	0.01501	9.763	650.5	473.66
		82.0	81.00	0.5612	0.00639	0.01317	10.653	809.0	454.04
		97.0	88.80	0.5200	0.00757	0.01199	10.639	887.0	461.24

Table 50 Rate Constants of the Formation Reaction (cont.)

Tabulation of $1/a$, $-b/a$, C_F for each rate experiment

Experiment number and temperature, minutes

Point of contact of tangent on curve Recip. resist. mhos $\times 10^5$

$\frac{d \text{ recip. resist.}}{dt} = \frac{\text{mhos}_2 - \text{mhos}_1}{t_2 - t_1} \times 10^5$

$1/a = 1.3504$
 $-b/a = 1.9806$
 $C_F = 0.03000$

R40-38

Elapsed time, minutes	Recip. resist. mhos $\times 10^5$	$\frac{d \text{ recip. resist.}}{dt} \times 10^5$
6.0	24.50	1.9954
20.0	46.50	1.3800
30.5	60.00	1.1531
56.0	86.00	0.9083

$1/a = 1.5726$
 $-b/a = 2.2577$
 $C_F = 0.02044$

R41-38

Elapsed time, minutes	Recip. resist. mhos $\times 10^5$	$\frac{d \text{ recip. resist.}}{dt} \times 10^5$
23.5	75.50	1.8117
40.0	100.00	1.5538
70.0	140.00	1.2556

$1/a = 1.5726$
 $-b/a = 2.2577$
 $C_F = 0.02957$

R42-38

Elapsed time, minutes	Recip. resist. mhos $\times 10^5$	$\frac{d \text{ recip. resist.}}{dt} \times 10^5$
16.5	78.50	2.8773
25.0	98.50	2.3395
50.0	150.00	1.7308

$1/a = 1.5726$
 $-b/a = 2.2577$
 $C_F = 0.04356$

R43-38

Elapsed time, minutes	Recip. resist. mhos $\times 10^5$	$\frac{d \text{ recip. resist.}}{dt} \times 10^5$
29.5	93.5	2.9857
52.5	146.5	2.0897
110.0	252.5	1.7570

$1/a = 1.5726$
 $-b/a = 2.2577$
 $C_F = 0.03750$

R44-38

Elapsed time, minutes	Recip. resist. mhos $\times 10^5$	$\frac{d \text{ recip. resist.}}{dt} \times 10^5$
22.5	97.5	2.4778
42.0	139.5	2.0984
53.0	163.5	1.8232
146.5	286.0	1.1912

$10^{-b/a}$
 $\text{recip. resist.}^{1/a}$

$C_F \cdot 10^{-b/a}$
 $\text{recip. resist.}^{1/a}$

$\frac{10^{-b/a}}{a}$
 $\text{recip. resist.}^{1/a}$

$\frac{10^{-b/a} \text{ recip. resist.}^{1/a}}{a(C_F \cdot 10^{-b/a} \text{ recip. resist.}^{1/a})}$

$K_1 \times 10^5$

0.00013	0.02987	7.012	234.8	468.43
0.00302	0.02698	8.777	325.4	449.03
0.00426	0.02873	9.598	373.0	430.05
0.00693	0.02306	10.886	472.0	428.70

0.00223	0.01821	4.643	254.9	461.84
0.00347	0.01697	5.454	321.3	499.2
0.00587	0.01457	6.607	453.5	569.4

0.00237	0.02720	4.748	174.6	502.26
0.00338	0.02618	5.406	206.5	483.06
0.00656	0.02301	6.878	298.9	517.41

0.00312	0.04044	5.248	129.8	387.41
0.00632	0.03724	6.787	182.2	380.85
0.01488	0.04207	9.268	220.3	387.05

0.00333	0.03417	5.375	157.3	389.83
0.00585	0.03164	6.599	208.5	437.60
0.00751	0.02999	7.228	241.0	439.44

0.01810	0.03569	9.954	278.9	332.25
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meaningful. However, when the induction period was long enough to provide a small section of the rate measurement graph in the region before the break it was found that the formation rate constants were of the right order of magnitude. In fact, some agreed satisfactorily with the results of experiments R1-⁷⁵ through R4-⁷⁵. The values of the rate constants for experiments R6-⁷⁵, R8-⁷⁵, R10-⁷⁵, and R13-⁷⁵ were 1.191, 3.385, 2.141, and $1.612 \times 10^{-5} \text{ min.}^{-1}$, respectively.

Experiments R23-⁶⁰ through R40-³⁸ were devised for the study of the formation reaction at several temperatures. All provided data for calculating the rate constants of the formation reaction either over the entire course of the measurement or until the decomposition reaction began to occur.

Experiments R23-⁶⁰, R25-⁶⁰ through R28-⁶⁰, R29-⁵⁰, and R33-⁵⁰ exhibited no break and provided regions from 550 to 900 minutes long at -60°C., and from 700 to 775 minutes long at -50°C. over which the rate constants of the formation reaction could be measured. The reaction rate constants were substantially invariant over these regions.

Experiments R24-⁶⁰, R30-⁵⁰ through R32-⁵⁰, R34-⁵⁰, and R36-³⁸ through R40-³⁸ exhibited breaks, but provided reasonably wide regions before the break over which to

measure the formation reaction rate constant. The region before the break in experiment R24⁻⁶⁰ was 400 minutes long, in experiments at -50°C. it was from 150 to 425 minutes long, and at -38°C. it was from 70 to 150 minutes long. The reaction rate constants were substantially invariant over these regions and agreed with the rate constants measured at the same temperatures in experiments in which the break did not occur.

Conductivity Cell No. 5 (Figure 76) was too crudely designed to serve as a cell in which to take rate measurement data of value; though again, in the pre-break regions, formation rate constants were obtained using this cell at -38°C. that were of the order of magnitude expected for the reaction at that temperature.

They varied from 330 to 570 x 10⁻⁵ min.⁻¹ in the fourteen sample calculations made using the data of experiments R41⁻³⁸ through R44⁻³⁸.

Post break values of the formation reaction rate constants.- The calculations of the rate constants of the formation reaction in the case of a number of experiments which exhibited a break were repeated at intervals from the beginning of the reaction, through the pre-break region in which the formation reaction only occurred, through the region of rapid reaction,

$\frac{1}{2}$ scale

Fig. 76

and beyond it into the region in which the slow reaction occurred again.

The question which arose was whether the process returned to the simple formation reaction after the hydrazine present was all consumed in the decomposition reaction, or whether the decomposition reaction continued along with the formation reaction, and, being much faster, consumed the hydrazine from the formation reaction as fast as it was produced. In the latter case the calculated value of the rate constant for the formation reaction would be expected to be three times the value in the former case since the formation of a mole of hydrazine would consume a mole of chloramine and its immediate decomposition would consume two more moles of chloramine. If the formation reaction occurred alone it should, of course, have the same rate constant in this region as in the region before the break.

It should be noted that in this region the chloramine in some cases is largely consumed. Since its concentration is measured by difference, $C_F - \text{conc. NH}_4\text{Cl}$, any uncertainty in the absolute value of either term makes a proportionally larger error in the calculated value of the concentration as the concentration becomes smaller. This is reflected in an increase in the uncertainty of those rate constants.

The results of the calculation of the formation rate constants in the terminal region of slow reaction are given in Table 51. For comparison with these values, the average values of the formation rate constants in the pre-break regions are provided. They are 3.152, 28.757, and $106.10 \times 10^{-5} \text{ min}^{-1}$ at -75, -60, and -50°C., respectively. It can be seen that the rate constants lie in a range which varies from one to three times the pre-break value in most cases.

Thus a clear distinction between the two possibilities suggested cannot be made on the basis of the data. It may be that when the calculated constants are about three times the pre-break constants, that any intermediates or catalysts that are needed for the decomposition reaction have not been entirely consumed along with the hydrazine, and the decomposition reaction can continue to occur along with the formation reaction. In cases where the constants are the same as the pre-break values these intermediates may have been depleted, so that the decomposition reaction is retarded. If this is the case, one might expect the reaction mixture to show a succession of breaks, each with its own induction period. The data of experiment R37-38 suggest that such might have been the case in this experiment, though one experiment alone does not

Table 51 Post Break Values of the Specific Reaction Rate Constants of the Formation Reaction in the Terminal Region of Slow Reaction

Expt. number	k_1 $\times 10^5$	NH ₂ Cl conc.
R10-75	5.11	large excess
R13-75	5.13	large excess
R14-75	20.1	large excess
R16-75	8.76	large excess
R17-75	3.02	large excess
R18-75	20.1	large excess
R19-75	16.3	large excess
R22-75	31.0	large excess
	12.0	large excess
Average value of k_1 in pre-break region at -75°C.		
	3.152	
R24-60	95.1	large excess
Average value of k_1 in pre-break region at -60°C.		
	28.757	
R30-50	337	large excess
	278	large excess
	273	medium excess
	319	medium excess
	296	medium excess
	314	small excess
	305	small excess
R31-50	296	medium excess
	269	medium excess
	212	small excess
	165	small excess
R32-50	302	medium excess
	91.5	small excess
	81.7	small excess
R34-50	163	large excess
	99.7	medium excess
	80.8	medium excess
Average value of k_1 in pre-break region at -50°C.		
	106.10	

provide conclusive evidence. In such cases, the excess chloramine is too small to create a new set of conditions that lead to a break in the time that usually remains before the termination of the experiment.

In experiments yielding values of the rate constants intermediate between one and three times the pre-break formation rate constants, intermediate conditions may prevail. Usually low values of the constant in the terminal region are associated with small excesses of chloramine.

Order of the Formation Reaction

It was assumed in the sections dealing with the specific reaction rate constants of the formation reaction, pages 276-279, that the formation reaction exhibited pseudo first order dependence on the chloramine concentration. This assumption was validated in that the rate constants calculated for the reaction using an expression based on this assumption were constant over the entire course of the reaction unless a break occurred (Table 50).

However it was considered that a more direct confirmation was needed, and the order of the reaction was tested by studying the effect of reactant concentrations.

Derivation of the expression used to test the order of the formation reaction.- Since ammonia is the solvent as well as a reactant in the process its concentration remains substantially constant so that the conditions of the experiment will only allow observation of the dependence of the rate on the chloramine concentration. Were the apparent order with respect to ammonia not zero, the plot of equation (36), derived under the assumption that this is so, would not yield a line of constant slope, "n".

The test equation expressed directly in terms of the data is derived in the following steps:

$$-\frac{d \text{ conc. NH}_2\text{Cl}}{dt} = + \frac{d \text{ conc. NH}_4\text{Cl}}{dt} = k (\text{conc. NH}_2\text{Cl})^n \quad (27)$$

Terms equivalent of those of equation (27) are expressed in equations (26), (33), and (34).

$$\text{conc. NH}_4\text{Cl} = B \text{ recip.resist.}^A \quad (26)$$

$$\text{conc. NH}_2\text{Cl} = C_F - B \text{ recip.resist.}^A \quad (33)$$

$$\frac{d \text{ conc. NH}_4\text{Cl}}{dt} = A B \text{ recip.resist.}^{A-1} \frac{d \text{ recip.resist.}}{dt} \quad (34)$$

The substitutions are made in equation (27).

$$A B \text{ recip.resist.}^{A-1} \frac{d \text{ recip.resist.}}{dt} = k (C_F - B \text{ recip.resist.}^A)^n \quad (35)$$

Equation (35) is expressed in log form and constants are collected into a single term.

$$(A - 1) \text{ recip.resist.} + \log \frac{d \text{ recip.resist.}}{dt} = n \log (C_F - B \text{ recip.resist.}^A) + \log \frac{k}{AB} \quad (36)$$

A plot of the function

$$(A - 1) \text{ recip.resist.} + \log \frac{d \text{ recip.resist.}}{dt}$$

against

$$\log (C_F - B \text{ recip.resist.}^A)$$

should give a straight line of slope, "n", and intercept, $\log \frac{k}{AB}$. The value of "n" is the order of the reaction with respect to the chloramine concentration, and should remain constant over the entire region investigated.

Observed order of the formation reaction.- A graph of these functions is provided in Figure 77. A separate straight line is obtained for each of the four temperatures at which the rate measurements were conducted. The straight lines are narrowly defined by the experimental points and have slopes that are close to the value 1.00. As measured from a large working graph, they are 1.07, 1.03, 1.00 and 1.00 at -75° , -60° , -50° , and -38°C. , respectively. Hence it is established that the order of the reaction with respect to the chloramine concentration is 1.00.

Logarithm of the rate of formation of ammonium chloride vs. the logarithm of the chloramine concentration for reaction I at temperature

Fig.77

The calculations leading to points used on the graph (Figure 77) are outlined in Table 52. The points are derived from values taken from the rate measurement data that were known to yield formation rate constants near the average values of the constant for each of the four temperatures.

Thermodynamic Constants of the Formation Reaction

The Arrhenius, or empirical, activation energy, E_a , was calculated for the formation reaction by use of the equation

$$\ln k = - \frac{E_a}{RT} + \text{constant.} \quad (37)$$

The rate constants at several temperatures were graphed to give the typical Arrhenius plot of logarithm of the rate constant against the reciprocal of the absolute temperature. The slope of the graph equals $-E_a/R$.

The graph is shown in Figure 78 and the data supporting the points are provided in Table 53. The exact values of the temperatures which for convenience have been called -75° , -60° , -50° , and -38°C . are -74.3° , -60.4° , -50.6° , and -37.9°C . The data of Hurley⁵⁹ are included for comparison. His work was performed at -33°C .

⁵⁹ Forrest Reyburn Hurley, "Studies in Nitrogen Chemistry," Ph.D. dissertation, The Ohio State University, 1954, p. 72.

Table 52 Order of the Formation Reaction

Calculations of data used in determining the order of the hydrazine forming reaction through a plot of the function $(A-1) \log \text{recip.resist.} + \log \frac{d \text{ recip.resist.}}{dt}$

against $C_F - B \text{ recip.resist.}^A$

Expt. number	$A = \frac{1}{a}$	$B = 10^{-b}$	C_F moles/liter $\times 10^3$	$\frac{d \text{ recip. resist.}}{dt}$ mhos/min. $\times 10^7$	Log of $\frac{d \text{ recip. resist.}}{dt}$	Recip. resist. mhos $\times 10^5$	Log of recip. resist.	(A-1) log of recip. resist.	A log of recip. resist.	Recip. resist. ^A $\times 10^6$	B recip. resist. ^A moles/liter $\times 10^3$	$C_F - B \text{ recip. resist.}^A$ moles/liter $\times 10^3$	Log of $(C_F - B \text{ recip. resist.}^A)$	(A-1) log of recip. resist. + log of $\frac{d \text{ recip. resist.}}{dt}$
R2-75	1.3667	207.014	15.78	.5643	-7.24849	7.55	-4.1220	-1.5115	-5.6336	2.3249	4.8128	15.297	-1.81539	-8.7600
R3-75	1.3667	207.014	16.39	.5552	-7.25555	8.50	-4.0706	-1.4927	-5.5633	2.7334	.56585	15.828	-1.80057	-8.7482
R4-75	1.3667	207.014	12.98	.4953 .3857 .3145 .2664	-7.30513 -7.41375 -7.50238 -7.57447	5.80 13.40 19.43 24.90	-4.2366 -3.8729 -3.7115 -3.6038	-1.5536 -1.4202 -1.3610 -1.3215	-5.7902 -5.2931 -5.0725 -4.9253	1.6217 5.0921 8.4626 11.877	.33558 1.0541 1.7512 2.4587	12.641 11.923 11.226 10.518	-1.89822 -1.92367 -1.94978 -1.97806	-8.8587 -8.8340 -8.8634 -8.8960
R23-60	1.3316	120.056	26.16	8.587 7.263 4.990	-6.06616 -6.13888 -6.30190	11.9 22.10 44.20	-3.92445 -3.65561 -3.35488	-1.3013 -1.2122 -1.1124	-5.2258 -4.8678 -4.4670	5.9457 13.552 34.119	.71352 1.6267 4.0945	22.739 24.531 22.064	-1.64323 -1.61028 -1.65631	-7.3675 -7.3511 -7.4143
R24-60	1.3316	120.056	23.45	7.389 6.456	-6.13141 -6.19004	16.70 23.30	-3.77728 -3.63264	-1.2525 -1.2046	-5.0298 -4.8372	9.3368 14.548	1.1205 1.7458	22.333 21.707	-1.65103 -1.66340	-7.3839 -7.3946
R25-60	1.3316	120.056	28.28	7.752 6.100	-6.11059 -6.21467	21.20 38.80	-3.67366 -3.41117	-1.2182 -1.1311	-4.8918 -4.5423	12.829 28.688	1.5396 3.4427	26.744 24.841	-1.57278 -1.60483	-7.3288 -7.3458
R26-60	1.3316	120.056	29.64	8.012	-6.09626	20.70	-3.68403	-1.2216	-4.9056	12.428	1.4914	28.144	-1.55062	-7.3179
R27-60	1.3316	120.056	29.62	9.432 8.179 5.300	-6.02540 -6.08730 -6.27572	17.30 21.80 53.55	-3.76195 -3.66154 -3.27124	-1.2475 -1.2142 -1.0847	-5.0094 -4.8757 -4.3560	9.7858 13.314 44.056	1.1744 1.5977 5.2869	28.477 28.023 24.334	-1.54597 -1.55249 -1.61379	-7.2729 -7.3015 -7.3604
R28-60	1.3316	120.056	19.83	7.137 5.195	-6.14648 -6.28441	8.75 23.30	-4.05799 -3.63264	-1.3456 -1.2046	-5.4036 -4.8372	3.9482 14.548	.4738 1.7458	19.355 18.083	-1.71320 -1.74273	-7.4921 -7.4890
R29-50	1.3432	113.053	27.08	20.79	-5.68215	55.25	-3.25767	-1.1180	-4.3757	42.102	4.7578	22.319	-1.65133	-6.8002

Table 52 Order of the Formation Reaction (cont.)

Expt. number	$A = \frac{1}{a}$	$B = 10^{-\frac{b}{a}}$	C_F moles/liter $\times 10^3$	d recip. resist. dt mhos/min. $\times 10^7$	Log of d recip. resist. dt	Recip. resist. mhos $\times 10^5$	Log of recip. resist.
R30 ⁻⁵⁰	1.3432	113.053	27.84	37.60 27.60	-5.42481 -5.55909	15.60 33.90	-3.80688 -3.46980
R32 ⁻⁵⁰	1.3432	113.053	23.25	32.76 29.64 25.76 22.67	-5.48466 -5.52812 -5.58905 -5.64455	14.20 18.15 25.20 33.10	-3.84771 -3.74112 -3.59860 -3.48017
R33 ⁻⁵⁰	1.3432	113.053	21.71	32.04 27.83 23.45 20.45	-5.49431 -5.55549 -5.62986 -5.68931	12.00 17.37 26.50 35.10	-3.92082 -3.76020 -3.57675 -3.45469
R34 ⁻⁵⁰	1.3432	113.053	29.87	37.25	-5.42887	17.80	-3.74958
R35 ⁻⁵⁰	1.3432	113.053	35.98	33.50	-5.47496	39.90	-3.39903
R36 ⁻³⁸	1.3504	95.632	19.87	96.40	-5.01592	36.70	-3.43533
R38 ⁻³⁸	1.3504	95.632	18.89	114.69 99.94 50.68	-4.94048 -5.00026 -5.29516	23.50 32.50 82.25	-3.62893 -3.48812 -3.08486
R39 ⁻³⁸	1.3504	95.632	19.56	143.67 105.00 56.12	-4.84269 -4.97881 -5.25088	15.50 31.00 81.00	-3.80967 -3.50864 -3.09151
R40 ⁻³⁸	1.3504	95.632	30.00	138.00	-4.86012	46.50	-3.33255

(A-1) log of recip. resist.	A log of recip. resist.	Recip. resist. ^A $\times 10^6$	B recip. resist. ^A moles/liter $\times 10^3$	C_F - B recip. resist. ^A moles/liter $\times 10^3$	Log of (C_F - B recip. resist. ^A)	(A-1) log of recip.resist. + log of d recip. resist. dt
-1.3065 -1.1908	-5.1134 -4.6606	7.7020 21.848	.87036 2.4687	26.972 25.373	-1.56909 -1.59563	-6.7313 -6.7499
-1.3205 -1.2840 -1.2350 -1.1944	-5.1682 -5.0251 -4.8386 -4.6746	67.888 9.4384 14.669 20.673	.76718 1.0668 1.6577 2.4462	22.542 22.182 21.591 20.803	-1.64701 -1.65400 -1.66573 -1.68188	-6.8052 -6.8121 -6.8240 -6.8390
-1.3456 -1.2905 -1.2275 -1.1862	-5.2664 -5.0507 -4.8043 -4.6403	5.4150 8.8982 15.693 22.893	.61193 1.0055 1.7734 2.5870	21.095 20.701 19.934 19.120	-1.67582 -1.68401 -1.70040 -1.72079	-6.8399 -6.8460 -6.8574 -6.8755
-1.2868 -1.1665	-5.0364 -4.5656	9.1960 27.189	1.0392 3.0726	28.328 32.902	-1.54019 -1.48277	-6.7157 -6.6415
-1.2037	-4.6391	22.956	2.1957	17.671	-1.75274	-6.2196
-1.2716 -1.2222 -1.0809	-4.9005 -4.7104 -4.1658	12.575 19.480 68.265	1.2025 1.8630 6.5283	17.687 17.026 12.361	-1.75234 -1.76889 -1.90794	-6.2121 -6.2225 -6.3761
-1.3349 -1.2294 -1.0836	-5.1446 -4.7381 -4.1748	7.1680 18.277 66.865	.68548 1.7478 6.3944	18.876 17.813 13.167	-1.72409 -1.74826 -1.87723	-6.1776 -6.2082 -6.3345
-1.1677	-4.5003	31.608	3.0227	26.975	-1.56904	-6.0278

Table 53 Calculation for Graph of Logarithm of K_1 vs. the Reciprocal of the Absolute Temperature

Average $K_1 \times 10^5$	Log K_1	Avg. deviation of a single observation	Number of observations	Exact temp. degrees C.	1/T
3.152	-4.50141	± 0.283	7	-74.3	0.0050302
28.757	-3.54126	± 1.198	31	-60.4	0.0047014
106.096	-2.97430	± 6.680	40	-50.6	0.0044944
448.935	-2.34781	± 16.868	23	-37.9	0.0042517
606.000*	-2.21753	± 12.000	14	-33.0	0.0041667

*Constants measured by Hurley

Plot of the logarithm of K_1 vs. the reciprocal of the absolute temperature

Fig.78

Average values of the reaction rate constants were used for each temperature. The number of individual constants averaged were 7, 31, 40, 23, and 14 at the five temperatures.

The calculated value of Arrhenius activation energy, E_a , was found to be 13.29 kcal. per mole. The relationship

$$H^\ddagger = E_a - RT \quad (38)$$

yields the values 12.90, 12.87, 12.85, 12.82, and 12.81 kcal. per mole for the heat of activation, $H^\ddagger$, at the temperatures -74.3° , -60.4° , -50.6° , -37.9° , and -33°C. , respectively.

The average value of the rate constants measured by Hurley at -33°C. constitutes a point on the graph which is in general agreement, though not in close agreement, with what this work predicts for that temperature. The difference may be attributed to a temperature error or to a difference in experimental procedure.

The entropy of activation was obtained from the expression for the specific reaction rate constant,

$$k = \frac{RT}{Nh} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad (39)$$

in which the terms have their customary meaning.

In the log form this relationship becomes

$$\begin{aligned} 2.303 \log \frac{k_{Nh}}{RT} &= \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \\ &= \frac{\Delta S^\ddagger}{R} - \frac{E_a - RT}{RT} \end{aligned} \quad (40)$$

This is solved for $\Delta S^\ddagger$.

$$\Delta S^\ddagger = 2.303 R \log \frac{k_{Nh}}{RT} + \frac{E_a - RT}{T} \quad (41)$$

The values of $\Delta S^\ddagger$ were found to be -22.06, -22.15, -22.38, -22.84, and -23.43 e.u. at -74.3°, -60.4°, -50.6°, -37.9°, and -33.0°C.

These values and the values of $\Delta H^\ddagger$ are consistent with the corresponding thermodynamic values calculated from rate measurements for similar displacement reactions of halogen ions by amines.⁶⁰

The Effect of Ammonium Chloride on the Rate of the Formation Reaction

The calculations of the specific reaction rate constants are summarized in Table 50. There the rate constant is recorded along with the reciprocal resistance of the solution at the point corresponding to which the rate constant was calculated.

In order to demonstrate the effect of ammonium chloride on the rate of the formation reaction, plots

⁶⁰ A. A. Frost and R. G. Pearson, Kinetics and Mechanism (New York, John Wiley and Sons, Inc., 1953), Table V, p. 128.

of the rate constants against reciprocal cell resistance were prepared from these data for each temperature at which the rates were measured.

Since the reciprocal resistance is related to the ammonium chloride concentration by the equation

$$\text{Conc. NH}_4\text{Cl} = B \text{ recip.resist.}^A, \quad (26)$$

it was considered an adequate test of the effect to plot the rate constants against the reciprocal resistance of the solution rather than against the ammonium chloride concentration itself.

Graphs are given in Figures 79 through 82 for the variation of the rate constants with reciprocal resistance at -75° , -60° , -50° , and -38°C ., respectively. On first glance it might seem that the rate constants are entirely unreliable, but actually the results are quite reproducible. The figures are drawn to emphasize the scatter of the points and to magnify any variation of rate constants with increase in the ammonium chloride content that may be inherent in the data. In the case of the graph of the constants measured at -38°C . (Figure 82), though the entire page is peppered with points, this scattering represents only a relatively narrow strip of the complete graph. The region shown is from $k = 420$ to $500 \times 10^{-5} \text{ min.}^{-1}$. Most of the points lie within

$\pm 30 \times 10^{-5} \text{ min.}^{-1}$ of the average value of the constant, or about $\pm 7\%$ of the maximum variation from the average. The extent of widest variation is only about $\pm 5\%$ of the average values of the constants at the lower temperatures.

The results show that there is no trend in the reaction rate with increase of ammonium chloride concentration unless it is small enough to be masked by the experimental error. The implications of this evidence are discussed in the section dealing with reaction mechanisms on pages **316-321**.

VARIATION OF K_1 WITH RECIPROCAL RESISTANCE OF THE REACTION MIXTURE

Fig. 79

VARIATION OF K_1 WITH RECIPROCAL RESISTANCE OF THE REACTION MIXTURE

Fig. 80

VARIATION OF K_1 WITH RECIPROCAL RESISTANCE OF THE REACTION MIXTURE

Fig.81

VARIATION OF K_1 WITH RECIPROCAL RESISTANCE OF THE REACTION MIXTURE
Fig.82

DISCUSSION

Mechanism of the Formation Reaction

Yields obtained in the preparation of hydrazine result from the net effect of the competitive reactions involved, the formation reaction and the decomposition reaction.

Because of the similarity of the Raschig synthesis in an aqueous solution of fixed base to the chloramine-ammonia process in anhydrous ammonia they are considered together in this discussion.

Several mechanisms have, in fact, been proposed to explain the phenomena observed, and, as is usually true in such cases, there is much that is common to each of them. This is to be expected, since much of the data which are presented in the support of one may equally well support the others.

Also it may be noted that conditions which increase the yield and are interpreted as favorable to the formation reaction, may, in fact, not affect it at all. Instead they may be unfavorable to the decomposition reaction which is occurring at the same time. Data presented as evidence in support of a mechanism will be examined in view of these considerations.

The mechanism of the formation reaction as proposed by Audrieth, Colton, and Jones.- A mechanism for the Raschig synthesis was proposed in the paper by Audrieth, Colton, and Jones⁶¹ to account for the experimentally observed factors affecting the yield of hydrazine.

Chloramine is formed according to the equation

In the presence of strong base it ionizes to form the chloramide ion,

since the inductive effect of chlorine labilizes an N-H bond. According to this mechanism the chloramide ion reacts slowly with the base, B, or, according to another variation of the mechanism, loses chloride ion to form the imide molecule which then reacts slowly with the base.

or

The base may be NH_3 , RNH_2 , R_2NH , or even water.

⁶¹ L. F. Audrieth, Ervin Colton, and M. M. Jones, "Formation of Hydrazine from t-Butyl Hypochlorite and Ammonia," Journal of the American Chemical Society, Vol. 76 (March 5, 1954), pp. 1428-1431.

After the addition reaction with the base the molecule is presumed to rearrange to hydrazine, in the case of the reaction with ammonia.

The mechanism of the formation reaction as proposed by Bodenstein, Cahn, and Powell.- The mechanism of Bodenstein,⁶² Cahn and Powell⁶³ proposed for the formation reaction as it occurs in the Raschig synthesis is as follows:

The mechanism of the formation reaction as proposed by Wiberg and Schmidt.- The mechanism of Wiberg and Schmidt⁶⁴ is predicted on the belief that water is essential for the formation of hydrazine from hypochlorite and ammonia or from chloramine and ammonia. Likewise, they believe that water is essential for the formation of nitrogen from hypochlorite and hydrazine or from chloramine and hydrazine. They do not regard

⁶² Max Bodenstein, "Monochloramin und Hydrazin. II Bildung von Hydrazine und Zersetzung von Monochloramin in ammoniakalischer Lösung," Zeitschrift für Physikalische Chemie, Vol. 139A (1928), pp. 397-415.

⁶³ J. W. Cahn and R. E. Powell, "The Raschig Synthesis of Hydrazine," Journal of the American Chemical Society, Vol. 76 (May 5, 1954), pp. 2565-2567.

⁶⁴ Egon Wiberg and Max Schmidt, "Ueber den Reaktionsmechanismus der Raschigschen Hydrazinsynthese," Zeitschrift für Naturforschung, Vol. 66 (1951), p. 336.

chloramine as the oxidant in the Raschig synthesis, but rather hypochlorous acid. The following steps constitute their mechanism for the formation reaction:

or

They write the equation for the decomposition of hydrazine as:

The mechanisms of Audrieth and his group, of Bodenstein, Cahn and Powell, and of Wiberg and Schmidt will be compared.

Effect of fixed base on the formation reaction.-

The first piece of evidence discussed is derived from work done in this laboratory.^{65, 66} It compliments the findings reported in this dissertation and should be summarized here.

⁶⁵ H. H. Sisler, C. E. Boatman, F. T. Neth, Robert Smith, Richard Shellman, and Donald Kelmers, "The Chloramine-Ammonia Reaction in Pure Water and in Other Solvents," Journal of the American Chemical Society, Vol. 76 (Aug. 5, 1954), pp. 3912-3914.

⁶⁶ R. S. Drago and H. H. Sisler, "The Effect of Hydroxide and Ammonium Ions on the Reaction of Chloramine with Aqueous Ammonia," Journal of the American Chemical Society, Vol. 77 (June 20, 1955), pp. 3191-3194.

It should be noted that the Audrieth group long held the belief that sodium hydroxide is essential in the Raschig synthesis of hydrazine. Though that view point has now been abandoned,⁶⁷ it had been regarded as evidence⁶⁸ that the acid ionization of chloramine is an essential step as proposed in the Audrieth mechanism. It had been concluded that the acid ionization of chloramine would be very slight, except in strongly basic solution, since the pK of chloramine had been estimated⁶⁹ at 14 ± 2 .

Sisler and coworkers⁷⁰ showed that hydrazine could be made in the absence of fixed base not only in anhydrous ammonia, but in aqueous ammonia and other solvents, though, as was pointed out by Jones, Audrieth, and Colton,⁷¹ yields were lower. However,

⁶⁷ M. M. Jones, L. F. Audrieth, and Ervin Colton, "Studies on the Raschig Synthesis of Hydrazine: The Reaction between Aqueous Chloramine and Ammonia Solutions," Journal of the American Chemical Society, pp. 2701-2703.

⁶⁸ L. F. Audrieth, Ervin Colton, and M. M. Jones, op.cit.

⁶⁹ W. L. Jolly, "The Thermodynamic Properties of Chloramine, Di-Chloramine, and Nitrogen Tri-Chloride," Journal of Physical Chemistry, Vol. 60 (April, 1956), pp. 507-508.

⁷⁰ H. M. Sisler, C. E. Boatman, F. T. Neth, Robert Smith, Richard Shellman, and Donald Kelmers, op.cit.

⁷¹ M. M. Jones, L. F. Audrieth, and Ervin Colton, op.cit.

Drago and Sisler⁷² showed that the best yields in the Raschig process could be obtained when the fixed base was just in excess of the ammonium chloride being formed in the reaction. This condition was achieved by the successive addition of small increments of base as the ammonium chloride was produced in the reaction mixture. They interpreted the high yields as due to the fact that excess base destroys chloramine according to the following equation:

According to the mechanism of Wiberg and Schmidt, equation (47), the presence of fixed base would reduce the concentration of hypochlorous acid presumed to be present and should reduce the rate of the formation reaction proportionally. It should have a similar effect on the decomposition reaction.

The magnitude of the effect on the two reactions and the consequent effect on yields in the Raschig synthesis is uncertain. Obviously the presence of fixed base according to this mechanism should have a definite inhibitory effect on the whole process. It is odd that such an effect has never been observed.

⁷² R. S. Drago and H. H. Sisler, op.cit.

As a matter of emphasis it may be stated that excess of fixed base is not essential to the formation of hydrazine. This fact constitutes evidence unfavorable to the Audrieth mechanism but is consistent with the Bodenstein, Cahn and Powell mechanism, which does not predict an effect due to fixed base. The inhibitory effect of fixed base predicted by the mechanism of Wiberg and Schmidt has never been observed.

Effect of ammonium chloride on the formation reaction.- The effect of ammonium chloride on the formation reaction can be used, just as was the presence of fixed base, to test the mechanisms proposed for the formation reaction.

It was known that the presence of ammonium chloride in the reaction mixture reduced the yields of hydrazine in the Raschig synthesis⁷³ and in the reaction in anhydrous ammonia.⁷⁴ It was thought by the adherents of the Audrieth mechanism that the ammonium chloride functioned to decrease the yields of hydrazine by suppressing the

⁷³ M. M. Jones, L. F. Audrieth, and Ervin Colton, op.cit.

⁷⁴ H. H. Sisler, F. T. Neth, and F. R. Hurley, "The Chloramine-ammonia Reaction in Liquid Ammonia," Journal of the American Chemical Society, Vol. 76 (Aug. 5, 1954), pp. 3909-3911.

acid ionization of chloramine. This was presumed to reduce the concentration of the chloramide ion and consequently to slow the formation reaction to such an extent that the decomposition reaction was favored.

Drago and Sisler⁷⁵ point out that this is possibly not the case, that the low yields of hydrazine in acid solution may be caused by the acid catalysis of the decomposition reaction instead. Thus they account for the need of only sufficient fixed base in the Raschig synthesis to neutralize the acid, ammonium chloride. The same undesirable effect of ammonium chloride had been reported in the synthesis in anhydrous ammonia.⁷⁶ The alternate interpretation by Sisler and Drago is consistent with the Bodenstein, Cahn and Powell mechanism, but there was no evidence available that could be used to decide which interpretation was correct.

That evidence was provided in the present work. The specific reaction rate constants of the formation reaction were measured at four temperatures over a tenfold range of ammonium chloride concentration, from .001 to .010 molar. The results are summarized in Table 50 and

⁷⁵ R. S. Drago and H. H. Sisler, op.cit.

⁷⁶ H. H. Sisler, F. T. Neth, and F. R. Hurley, op.cit.

Figures 79 through 82. A description of the results is given on pages 303-305.

It was shown for more than a score of independent reaction mixtures that over the entire course of the formation reaction the specific rate constants are independent of the ammonium chloride concentration. The rate constants were measured over a wide extent of reaction in an environment continually increasing in ammonium chloride concentration, from the beginning of the reaction until the decomposition reaction intervened, or, in those cases where the decomposition reaction did not occur, over the whole course of the reaction. The time of observation varied from 7,200 minutes at the lowest temperature to 50 minutes at the highest. These values were found to be constant within less than five percent of the average value of the constant over the whole course of the reaction, with an altogether random scattering of points, within the limits mentioned, at the temperatures of -75° , -60° , -50° , and -38°C .

The work reported by Hurley⁷⁷ confirms this observation. He found for more than a dozen independent reaction mixtures at -33°C . that the rate constants of

⁷⁷ Forrest Meyburn Hurley, "Studies in Nitrogen Chemistry." Ph.D. dissertation, The Ohio State University, 1954, p. 72.

the formation reaction, within the first hour or two, which is the interval over which he made calculations, were unaffected by the presence of ammonium chloride in amounts varying from 0.001 to 0.009 molar, a change in acidity of ninefold. The standard deviation of the rate constants for these observations was about three percent. Thus it was confirmed that ammonium chloride concentration does not affect the rate of the formation reaction within the experimental error of the measurements.

If the mechanism of the Audrieth group applies to the formation reaction, a tenfold change in ammonium chloride concentration should make a tenfold change, in the opposite sense, in the concentration of the chloramide ion. This is indicated by application of the law of mass action to the ionization equilibrium of chloramine.

$$K = \frac{[\text{NHCl}^-][\text{NH}_4^+]}{[\text{NH}_2\text{Cl}][\text{NH}_3]} \quad (53)$$

It should be noted that the concentration of ammonia is practically invariant, that the concentration of chloramine is large compared with that of the chloramide ion, and that the concentration of ammonium chloride was changed tenfold. The resultant extensive change in the chloramide ion concentration and in the derived

NH species should have produced a many fold change (500-1,000 percent) in the rate of the formation reaction, that could in no sense be masked by a 3-5 percent experimental error. But such was not the case.

Since it would require large quantities of acid to alter the concentration of ammonia appreciably, the Bodenstein, Cahn and Bowell mechanism, equation (10), does not predict an effect due to the presence of an acid.

In summary, it can be pointed out that this work has shown that the formation reaction is unaffected by the presence of ammonium chloride. The fact is confirmed by the work of Hurley. This evidence is consistent with the mechanism of Bodenstein, Cahn and Bowell, and is inconsistent with the mechanism of the Audrieth group. This evidence leads to the acceptance of the explanation of Drago and Sisler⁷⁸ concerning the manner in which ammonium chloride reduces yields in the synthesis of hydrazine. The evidence is also consistent with the complimentary fact already noted that fixed base is not essential in the Raschig synthesis.

The effect of ammonium chloride on yields in the Raschig synthesis and in the synthesis in liquid

⁷⁸ R. S. Drago and H. H. Sisler, op.cit.

ammonia cannot be used to test the validity of the mechanism of Wiberg and Schmidt because it will have a similar effect on both the formation and decomposition reactions. The effect of the acidic substance, ammonium chloride, according to their mechanism, should be expected to be opposite to the effect of excess of fixed base in the Raschig synthesis, i.e., it should increase the concentration of unionized hypochlorous acid and should have an accelerating effect on the entire process. The relative magnitude of the acceleration on the two reactions will determine its effect on yields.

The effect of change of solvent on the rate of the formation reaction.- Though yield data offer no means of testing the mechanism of Wiberg and Schmidt, comparison of the rate of the reaction in different solvents should provide the means. Use will be made of the measurement of the absolute rate of the formation reaction in liquid ammonia reported in this dissertation.

It would be expected according to this mechanism that the reaction in liquid ammonia would be much less rapid than in water since, for two reasons, the quantity of the active species, hypochlorous acid, would be less.

First, the quantity of water available for hydrolysis is quite limited. A high estimate of the water

content of the liquid ammonia solutions being 0.5 percent, or 0.03 molar. This should certainly restrict the hydrolysis of chloramine.

Second, the neutralization of any hypochlorous acid formed would be much more extensive in ammonia than in water and the concentration of the hypochlorous acid, as opposed to the concentration of ammonium hypochlorite, would be much less than in water solution.

A rough comparison of rates in concentrated aqueous ammonia and in liquid ammonia is possible from available experimental data.

It was reported by Sisler, Boatman, Neth, Smith, Shellman, and Kelmers⁷⁹ that the reaction between chloramine and ammonia in saturated ammonia solutions in pure water appears to be over in less than five minutes at room temperature. Drago and Sisler⁸⁰ state that in reaction mixtures of the Raschig synthesis the reaction is over in less than fifteen minutes at 24°C. These are rough estimates and represent times within which the experimenters were certain of obtaining complete reaction. Calculations made using the temperature coefficient

⁷⁹ H. H. Sisler, C. E. Boatman, F. T. Neth, Robert Smith, Richard Shellman, and Donald Kelmers, op.cit.

⁸⁰ A. S. Drago and H. H. Sisler, op.cit.

determined in this dissertation show that the half life of the formation reaction in liquid ammonia solution is about 0.3 minutes at 27°C. The reaction in liquid ammonia at that temperature (autoclave) would certainly be over in one or two minutes, even neglecting the contribution from the decomposition reaction. From these data it seems that the rates in the two solvents are of comparable orders of magnitude at equal temperatures, or, perhaps, that the rate in liquid ammonia is faster. This evidence is certainly unfavorable to the mechanism of Wiberg and Schmidt which, as was mentioned above, anticipates a very much slower reaction in liquid ammonia than in aqueous ammonia.

The kinetic salt effect.- The possibility that the kinetic salt effect accounts for the decrease in yield produced by ammonium chloride in the synthesis of hydrazine is unlikely. This view is taken in as much as in neither this work nor in that of Hurley⁸¹ was a drift perceived in the rate constants of the formation reaction with an approximately tenfold change in the concentration of ammonium chloride.

Neither the mechanism of Bodenstein, Cahn and Powell nor of the Audrieth group, however, anticipates such an effect, whether, in the latter case, the

⁸¹ Forrest Keyburn Hurley, op.cit.

slow step is between the imide molecule and ammonia, equation (46), or between the chloramide ion and ammonia, equation (44).

Of course, this does not rule out the possibility that there is a kinetic salt effect which acts to increase the rate of the decomposition reaction and thus to decrease the yield of hydrazine. However, the following evidence does preclude such an interpretation.

The yield studies of Jones, Audrieth, and Colton⁸² are summarized in a most convincing graph, their Figure 2, in which the effects on the Raschig synthesis of sodium chloride, also a 1-1 electrolyte, are shown to be negligible, whereas equivalent ammonium chloride concentrations reduce the yield substantially to nothing. This effect of ammonium chloride on the yields in the Raschig synthesis duplicates the findings of Drago and Sisler⁸³ as shown in their Figure 3.

The combination of the kinetic studies reported here and in Hurley's dissertation with the yield data of Jones, Audrieth, and Colton and of Drago and Sisler indicate that the effect of ammonium chloride on the synthesis of hydrazine is produced through an acid

⁸² M. M. Jones, L. F. Audrieth, and Ervin Colton, op.cit.

⁸³ R. S. Drago and H. H. Sisler, op.cit.

effect rather than a salt effect and the reduction in yield must be caused by the acid catalysis of the decomposition reaction as suggested by Drago and Sisler.⁸⁴

The order of the formation reaction.- It was shown in this investigation and reported on pages 293-297 and in Figure 77 and in Table 52 that the formation reaction is pseudo first order, i.e., zero order with respect to ammonia and first order with respect to chloramine concentration. As was pointed out on these pages the experimental conditions do not permit the observation of the molecularity with respect to ammonia since it is both the solvent as well as the reactant and its concentration remains substantially invariant during the rate measurements.

A distinction between the mechanism of Bodenstein, Cahn and Powell and that of the Audrieth group cannot be made on the basis of this experimental evidence since, in this particular, both mechanisms overlap.

The Bodenstein, Cahn and Powell mechanism,

proposed to account for the yield data of the Raschig synthesis, predicts the reaction to be second order in the Raschig process, i.e., first order with respect to the concentrations of both chloramine and ammonia.

In the process in liquid ammonia it predicts it to be pseudo first order, i.e., zero order with respect to ammonia and first order with respect to chloramine. The fixed base of the Raschig process is replaced by ammonia in the process in liquid ammonia.

The slow step in the mechanism of the Audrieth group is provided in equation (44) or (46),

Either of these predicts the same kinetics as does the Bodenstein, Cahn and Powell mechanism, but both equation (44) and (46) suffer in the manner indicated from being dependent on acid ionization of chloramine.

Quaternary hydrazinium salts, intermediates of the formation reaction.- Certain synthetic work performed in this laboratory has strong bearing on the understanding of the mechanism underlying these kinetic studies and is reported here for that reason.

Omiotanski and Sisler⁸⁵ report that chloramine reacts with anhydrous tertiary amines to form the corresponding 1,1,1-trisubstituted hydrazinium chlorides. This discovery constitutes a point in support of the Bodenstein, Cahn and Powell mechanism, since it is

⁸⁵ G. M. Omietanski and H. H. Sisler, "The Reaction of Chloramine with Tertiary Amines. 1,1,1-Trisubstituted Hydrazinium Salts," Journal of the American Chemical Society, Vol. 78 (March 20, 1956), pp.1211-1213.

found possible, thus, to isolate the product postulated by the theory, unchanged by further reaction.

With primary and secondary amines it happens that the quaternary hydrazinium salt predicted by the Bodenstein, Cahn and Powell mechanism, exchanges hydrogen chloride with the excess of unreacted amine, equations (55) and (56),

Thus it is not possible to observe the first product.

The reaction for a primary amine written in terms of the Audrieth mechanism is as follows

According to the Audrieth mechanism it is difficult to identify the intermediate in the case of the synthesis of primary and secondary amines because the rearrangement presumed to follow the addition reaction transforms it to the substituted hydrazine. But the ambiguity as to the nature of the intermediate is resolved in the case of reaction of chloramine with the tertiary amine. The

Audrieth mechanism would predict the appearance of one of the species shown, intermediate I or II, or final product, III.

I

II

III

Intermediate I or II would be expected depending on whether the reaction actually went through the steps predicted in equation (44) or equations (45) and (46). Product III would be expected if rearrangement of the intermediate occurred. Actually, no one of these was observed, but the first product predicted by the Bodenstein, Cahn and Powell mechanism, $\left[\begin{array}{c} \text{R H} \\ \text{RN-NH} \\ \text{R} \end{array} \right]^+ \text{Cl}^-$,

was obtained. The use of the identifiable alkyl radicals in place of hydrogen atoms locates the position of the substituents on the hydrazine skeleton, so that the last rearrangement, as assumed in the Audrieth mechanism must not have occurred, and the true nature of the intermediate is revealed.

Of course it is possible to have formed the intermediate I or II and then to have gained a proton from ammonia or ammonium ion present in the solution to form the hydrazinium compound. The loss and gain of

protons to and from the environment could convert a species of the type $\begin{array}{c} \text{H} \quad \text{H} \\ \text{H} \text{N} - \ddot{\text{N}}\text{H} \end{array}$ to $\begin{array}{c} \text{H} \quad \text{H} \\ \text{H} \text{N} - \text{N}\text{H} \end{array}$ during the formation of the less highly substituted hydrazines.

Mechanism of the Decomposition Reaction

In both the Raschig synthesis of hydrazine and in the synthesis in liquid ammonia, two reactions are encountered, the formation reaction, equation (7) and the decomposition reaction, equation (9).

As was pointed out on pages 13-16, it is the study of the kinetics of these reactions that is the subject of this work. Because of the complicated nature of the decomposition reaction a detailed knowledge of its kinetics was not achieved as was done in the case of the formation reaction. The formation reaction exhibited a remarkable text-book like conformity to the kinetics of the pseudo first order reaction. In the case of the decomposition reaction, however, much new information was obtained which should be of help in interpreting yield data and in selecting the best conditions for synthesis. The eccentricities of the decomposition reaction were revealed in a manner that the study of Cahn and Powell,⁸⁶ based on yield data alone, did not

⁸⁶ J. W. Cahn and R. E. Powell, op.cit.

even suggest.

As was pointed out on pages 88-97 and 108-115, and in Tables 5, 6, and 7, the stoichiometry of the decomposition reaction in liquid ammonia, equation (9), was established.

The method of calculating concentrations in the reaction mixture was explained on pages 99-108. In order for this method to be applicable, chloramine should be present in stoichiometric excess of the hydrazine. This was approximately the case in experiment R35-⁵⁰, in which the final corrected reciprocal resistance was just greater than the end concentration of the decomposition reaction.

The rate data are represented graphically by plots of reciprocal cell resistance against elapsed time. However, there is no great difference in the appearance of the graphs when concentrations of ammonium chloride are plotted against elapsed time. This point is confirmed if Figures 61 and 62, and 69 and 70 are compared. For simplicity in graphing, reciprocal cell resistance was plotted, but conclusions drawn from inspecting such figures are not misleading because of this selection of coordinates. However, in calculations of rate constants and other derived data,

the readings from the graphs were always converted to concentrations of ammonium chloride as the first step in the calculations.

Evidence of the isolation of the formation reaction from the decomposition reaction in pre-break regions.-

The evidence is abundant that the isolation of the formation reaction from the decomposition reaction in pre-break regions has been achieved and is summarized here for convenience. It was a fault⁸⁷ in earlier kinetic studies that the reactions were not separately studied.

In the present work, when it was desired to study the formation reaction, chloramine in low concentrations, but no hydrazine, was added to liquid ammonia. The decomposition reaction passed through a period of induction before it became effective and it was during this period that the formation reaction was observed to occur virtually alone. When it was desired to study the decomposition reaction, chloramine and hydrazine, both in low concentrations, were added to liquid ammonia. Also the formation reaction was greatly retarded by reducing the temperature of the reaction mixture to -75°C . Under these conditions, after a much shorter period of induction, in most cases (Experiments R5⁻⁷⁵ through R22⁻⁷⁵) the decomposition reaction began and

⁸⁷ Max Bodenstein, op.cit.

completely obscured the effect of the formation reaction. Of course at higher temperatures a correction for the formation reaction was needed.

The first point of evidence that only the formation reaction is occurring before the break is that the rate constants calculated for the formation reaction are constant over the entire course of the reaction, from the very beginning until it is terminated by the experimenter after 500 to 900 minutes. If the break intervenes, in the pre-break region the reaction exhibits the same rate constant as was found for other rate experiments at the corresponding temperature in which no break occurred. This discussion is amplified on pages 279, 287, and 288.

It was shown on pages 288-293 and in Table 51 that in the region of slow reaction following the rapid reaction, the rate constant reverts to one to three times the pre-break value of the formation rate constant. This is taken as evidence that there is a mixture of the formation and decomposition reactions occurring together in this region. The value $3k_{\text{formation}}$ corresponds with the case in which the hydrazine is consumed as fast as it is formed. This information suggests that the pre-break rate constant is characteristic of the limiting case in which the formation reaction only is occurring.

Over the course of the pre-break region hydrazine is continually forming. This fact is evidenced by the post break rise in the ammonium chloride concentration being twice the pre-break rise in ammonium chloride concentration. If the decomposition reaction were occurring before the break, it would be expected to consume some of the hydrazine formed before the break and the post break rise would not be as high.

The sudden departure from the established course of the reaction (the "break") demands some explanation. The explanation might be that the pre-break reaction, whatever it may be, has suddenly been accelerated by a catalyst, but otherwise its nature has not been altered. This is unlikely, for, when the fast reaction is over, the hydrazine which is formed before the break has been consumed. This constitutes, in fact, the occurrence of the decomposition reaction after the break.

The evolution of nitrogen indicated for the decomposition reaction, equation (9), is not observed to occur until the reciprocal resistance has begun to change rapidly following the break. Though this might be taken as evidence that saturation of the solution with nitrogen is not rapidly achieved, it should be noted that much nitrogen has already been bubbled through the solution during the preparation of a

solution of uniform composition. This should have brought the solution near to saturation. Therefore, the evolution of nitrogen is taken to mark the onset of the decomposition reaction.

It may be noted that the evolution of nitrogen usually follows the increase in conductivity at the break by a definitely observable period of time, one-half to one minute, and that then it is evolved in great quantity throughout the body of the solution and from the walls of the container. In pre-break regions, fifty to almost a thousand minutes have been observed to elapse without the evolution of any nitrogen. Again, this fact is taken as evidence that the decomposition reaction does not occur to any appreciable extent until after the break.

The rate of the formation reaction is relatively small at -75°C . as can be seen by inspection of Figures 32 through 36 accompanying Experiments R1-75 through R4-75. When the decomposition reaction superimposes itself upon the formation reaction as it does in Experiments R5-75 through R22-75, it produces ammonium chloride at such a rate that by comparison the contribution from the formation reaction is of little significance. Thus the decomposition reaction can be observed practically uncomplicated by the formation

reaction. At higher temperatures a correction must be applied for the formation reaction.

In summary, it can be stated that there is much evidence that the formation and decomposition reactions have been isolated from one another in such a manner that the slower and more easily obscured formation reaction proceeds substantially alone in the pre-break region and can be measured; and that the fast decomposition reaction, at low temperatures, can be observed with almost no interference from the slow formation reaction.

Comparison of the temperature coefficient of the formation and decomposition reactions.- The temperature coefficient of the formation reaction was measured and was found to be large, the Arrhenius activation energy, E_a , being 13.3 kcal. The fact that higher yields of hydrazine have been obtained at higher temperatures in liquid ammonia⁸⁸ can be explained by assuming a lower temperature coefficient for the decomposition reaction than for the formation reaction. An inspection of the rate measurement graphs at several temperatures, Figure 36 (formation, $-75^{\circ}\text{C}.$) and 37 (decomposition, $-75^{\circ}\text{C}.$), 53, 59, and 68, shows that the rate of formation of ammonium chloride in the pre-break region gets larger

⁸⁸ H. H. Sisler, F. T. Neth, and F. R. Hurley, op.cit.

with increase of temperature. It increases rapidly from an almost negligible value at -75°C . in comparison with that in the post break region at -75°C . until at -38°C . it equals about ten percent of the post break rate at -38°C .

It can also be observed by inspecting a large number of graphs covering all the temperatures studied that the decomposition reaction does not seem to be much faster at the higher temperatures than at the lower temperatures. However, it should be noted that when the curve is quite steep, it is difficult to estimate an increase in slope since an appreciable change in slope makes little angular change of the line on the graph.

Though rate constants were not obtained for the decomposition reaction this visual comparison of temperature dependence of the two reactions makes it clear that the decomposition reaction is not nearly so much affected by changes in temperature as is the formation reaction.

The effect of concentration on yields.- It was reported by Sisler, Neth, and Hurley⁸⁹ that higher yields of hydrazine are formed in liquid ammonia

⁸⁹ H. H. Sisler, F. T. Neth, and F. R. Hurley, op.cit.

solutions at lower concentrations of chloramine (lower mole ratios of chloramine to ammonia).

Obviously the explanation of this effect is that the concentration of the hydrazine formed will be low also. The loss through the decomposition reaction, depending as it does on both concentrations, will be small.

The kinetic studies revealed the unsuspected additional reason for higher yields at lower concentrations. They revealed the existence of an induction period in the course of the decomposition reaction. Further, Experiments R5-75 through R22-75 showed that the decrease in the concentration of chloramine and hydrazine lengthen the induction period. In some twenty-five preliminary experiments not reported in this dissertation in which larger quantities of hydrazine were used, the processes began with the decomposition reaction in full progress. The induction period in those cases could not be observed at all.

During the longer induction period that precedes the decomposition reaction in the more dilute solutions, the formation reaction has an opportunity to proceed for such a long time that the chloramine is too limited in amount then to consume all the hydrazine formed before the break. Such is approximately the case in Experiments R35-50, R38-38, R39-38, and 42-38.

Factors affecting the length of the induction period of the decomposition reaction.- As was pointed out in the preceeding section, the induction period is lengthened by decreasing the concentration of the reactants, chloramine and hydrazine.

Duplicate experiments exist in which the break occurs in one and not the other, for example, in Experiments R24⁻⁶⁰ and R28⁻⁶⁰. This lack of reproducibility indicates that factors other than concentrations of known reactants are involved in determining the length of the induction period. These factors possibly include the presence of metal catalysts or of ammonium chloride, the formation of intermediate substances, and the shift of the reaction from largely heterogeneous to largely homogeneous character depending on the surface condition of the reaction vessel.

The possibility that the break occurred because of contamination of the solution from metal ions derived from the mercury pools in the side arms of the conductivity cell was eliminated by performing some experiments in Conductivity Cell No.5 (Figure 76). This cell was constructed with mercury free side arms, but reactions carried out in it, none-the-less, exhibited the characteristic break in rate. See graphs of

Experiments R41⁻⁷⁵ through R44⁻⁷⁵. Electrode spacings, liquid levels, etc. were not reproducible enough in this cell to render it useful for anything other than to check this point.

Experiments R14⁻⁷⁵ through R18⁻⁷⁵ were performed to demonstrate the effect of increasing ammonium chloride concentration on the length of the induction period. No correlation was observed.

Proposed mechanism of the decomposition reaction.-

The mechanism proposed for the decomposition reaction in liquid ammonia should be such as to explain the observed phenomena as closely as possible. It should reproduce the measured stoichiometry of the reaction. It should predict an induction period for the reaction. It should account for the observed variable time of the onset of the reaction, and should explain the effect of a change in concentration of the reactants on the length of the induction period. It should account for the speed of the reaction, for its insensitivity to temperature changes and for the observed rates of reaction. A free radical mechanism is suggested to account for these phenomena.

The mechanism may be presented in a series of steps.

a. Hydrazine formation. This step is repeated here for convenience of reference.

b. Triazane formation. To account for the period of induction an intermediate substance, triazane, is thought to be accumulated slowly in the solution. The process parallels in mechanism, but necessarily follows, the formation of hydrazine.

The concentration of known reactants, chloramine and hydrazine, would decide the rate with which the intermediate was accumulated, and hence account for their effect on the length of the induction period.

c. Chain initiation. The chain carrier is postulated to be the amide radical, $\text{NH}_2^\bullet$. This radical is formed in an environment in which it is not likely to be consumed, since probable reactions which it may undergo regenerate it. Of course, this is the case in the reactions proposed for propagating the chain. Other reactions are

Chain initiation may occur as a homogeneous and/or surface catalyzed reaction of the intermediate, triazane.

To account for the possible effect of metal ion catalysts which may initiate the chain reaction at variable times, depending on their concentrations, the steps outlined in equations (65) and (66) are included.

The effect of ammonium chloride on yields has led Sisler and Drago⁹⁰ to suggest that the decomposition reaction is acid catalyzed. Therefore, a step is included in the mechanism which indicates that ammonium ion hastens chain initiation through shifting the equilibrium of equation (61) to the triazinium ion which can initiate the chain reaction.

This step would predict that addition of ammonium ion will decrease the length of the induction period. The results of Experiments R14⁻⁷⁵ through R18⁻⁷⁵ demonstrate no correlation between the ammonium chloride concentration and length of induction period. Possibly this effect was masked by other effects. Or, perhaps, the action of ammonium chloride is to be sought in its effect on the rate of the chain process.

⁹⁰ R. S. Drago and H. H. Sisler, op.cit.

d. Chain propagation. The free radical chain reaction is presumed to be carried by the amide radical, $\text{NH}_2^\bullet$, which abstracts hydrogen from hydrazine.

The NHNH_2 radical abstracts chlorine from chloramine and regenerates the chain carrier, $\text{NH}_2^\bullet$.

Ammonia removes the elements of hydrogen chloride leaving the diazene molecule.

Chloramine oxidizes the diazene molecule to nitrogen.

The net effect of these steps is to consume one molecule of hydrazine by two molecules of chloramine through the agency of the chain carrier $\text{NH}_2^\bullet$ and to form one molecule of nitrogen and two molecules of ammonium chloride. These results conform to the established stoichiometry of the decomposition reaction.

It should be noted that the nitrogen atoms originally contained in the hydrazine remain united in this process and form the end product chloramine. Exception is made of the atoms of nitrogen used to form triazane. These will be mixed in the products. If it is desired that this mechanism predict substantially no scrambling of nitrogen atoms in the process it is only necessary to suppose that relatively few molecules

of triazane are used in initiating the chains which are themselves of relatively great length. It should be noted in such a case that the nitrogen in chloramine ends up in the form of ammonium chloride.

It is reported by W. C. E. Higginson and D. Sutton⁹¹ as a result of studies using isotopically marked hydrazine that there is no scrambling of nitrogen in the oxidation of hydrazine observed in alkaline solution. The mechanism proposed in this dissertation thus conforms to their experimental results if, as has already been suggested, the chains are thought to be long.

They and also Cahn and Powell⁹² following a similar technique arrive at a mechanism which for the oxidation of hydrazine under these conditions leads from hydrazine by oxidation to the hydrazyl radical, HNNH_2 . The latter is oxidized further to diazene, HN=NH , which suffers rapid oxidation to nitrogen. This mechanism predicts no randomization of isotopic nitrogen but has the defect that it does not predict properties usually associated with chain reactions - such as the low temperature coefficient and the induction period found in the present work.

⁹¹ W. C. E. Higginson and D. Sutton, "The Oxidation of Hydrazine in Aqueous Solution. Part II. The Use of ^{15}N as a Tracer in the Oxidation of Hydrazine," Journal of the Chemical Society (London) Vol. 287 (1953). pp. 1402-1406.

⁹² J. W. Cahn and R. E. Powell, op.cit.

The three mechanisms of Kirke and Browne⁹³ for the oxidation of hydrazine under most conditions are non-chain processes. They involve among them six hydro-nitrogen intermediates, including diazene, tetrazane and two tetrazenes. They do not predict the several extents of randomization of isotopic nitrogen observed by Cahn and Powell⁹⁴ using a variety of oxidizing agents at several acidities.

e. Chain termination. Chain termination is effected through the combination of two of the chain carrying radicals.

It has been pointed out at appropriate points during the statement of the mechanism how the mechanism predicts the phenomena observed in the laboratory.

Evaluation of rates.- An explanation of so complicated a reaction as the decomposition reaction necessarily involves several steps. Often a number of choices are available which seem equally correct in accounting for a given step in the process. If rates predicted by the mechanism should agree with the experimentally

⁹³ R. E. Kirke and A. W. Browne, "Oxidation of Hydrazine. VIII. Mono-Deelectronators and Di-deelectronators," Journal of the American Chemical Society, Vol. 50 (Feb., 1928), pp. 337-347.

⁹⁴ J. W. Cahn and R. E. Powell, "Oxidation of Hydrazine in Solution," Journal of the American Chemical Society, Vol. 76 (May 5, 1954), pp. 2568-2572.

observed rates it would be a fortuitous circumstance in most cases. Likewise, the temperature dependence of the process is difficult to predict since it is a complicated function of the rate constants of the several reactions. As an ultimate complication, this reaction shows evidence of being in part heterogeneous. This is indicated by the results of experiments with near equal concentrations of known reactants which exhibit a break in one experiment (Experiment R24⁻⁶⁰) and not in the other (R28⁻⁶⁰). A mechanism proposed for a homogeneous process cannot be expected to predict rates for a process which in part is heterogeneous.

A number of attempts were made to find a simple relation between the concentrations of reactants and the observed rates of the decomposition reaction. The most nearly successful of these are reported here and the results are represented graphically in Figure 83.

It was assumed that the rate of the decomposition reaction might be expressed by equation (73).

$$\frac{d \text{ conc. } \text{NH}_4\text{Cl}}{dt} = k_{\text{decomposition}} \text{ conc. } \frac{1}{\text{NH}_2\text{Cl}} \text{ conc. } \frac{m}{\text{N}_2\text{H}_4} \quad (73)$$

The assumption was tested by a graphical method which was applied to the region of rapid reaction just beyond the break. Concentrations of chloramine and hydrazine were computed in this region for the series of Experiments

R5⁻⁷⁵ through R22⁻⁷⁵. These experiments were selected for the test because they were carried out at -75°C., a temperature at which the formation reaction offered little interference with the decomposition reaction. In order to cause the decomposition to occur at this temperature with a reasonably short induction period it was necessary to add weighed quantities of hydrazine to the reaction mixture.

In order to eliminate any effect due to change in ammonium chloride concentration, all the points selected for the calculations were chosen at equal ammonium chloride concentration.

A preliminary plot of the concentration of hydrazine against the corresponding concentration of chloramine was prepared. Beside each point on the graph the value of the rate of change of the reciprocal resistance of the reaction mixture was noted. If equation (73) had been applicable to the data it was expected that the largest values of the rate of change of reciprocal resistance would appear beside points located in the upper right hand corner of the figure and the smallest values would be found in the lower left hand corner. On a given horizontal line points of equal hydrazine concentration and varying chloramine concentration would be located. On a given vertical line points of equal chloramine concentration and varying hydrazine

concentration would be located. From data taken from the vertical line it would be possible to constitute a plot of the log of the time rate of change of ammonium chloride concentration against the log of the hydrazine concentration at constant chloramine and ammonium chloride concentration. From the slope of the line the order, "m", of the hydrazine concentration shown in equation (73) could be obtained. In a similar fashion data taken from the horizontal line could be used to determine the order, "l", of the chloramine concentration. It should be noted that there are families of horizontal and vertical lines, and, in principal, the order with respect to concentration could be tested over all regions investigated experimentally.

Equation (73) can be expressed in terms of the relation between concentration of ammonium chloride and the reciprocal resistance established by the cell calibration. Use is made of the method of calculating concentrations in the region of rapid reaction beyond the break described on pages 99-108.

Equation (26),

$$\text{conc. NH}_4\text{Cl} = B \text{ recip. resist.}^A, \quad (26)$$

is differentiated to give a relation between the time rate of change of concentration of ammonium chloride and the time rate of change of reciprocal resistance.

$$\frac{d \text{ conc. } \text{NH}_4\text{Cl}}{dt} = AB \text{ recip.resist.}^{A-1} \frac{d \text{ recip.resist.}}{dt} \quad (34)$$

Substitution of the concentrations in equation (73), properly expressed in terms of the experimental data, gives equation (74).

$$AB \text{ recip.resist.}^{A-1} \frac{d \text{ recip.resist.}}{dt} = k_2 (C_F - B \text{ recip.resist.})^1 \left(\frac{B \text{ recip.resist.}^A \text{ end rapid reaction} - B \text{ recip.resist.}^A}{2} \right)^m \quad (74)$$

In the log form equation (74) becomes, after collecting constant terms,

$$\begin{aligned} (A-1) \log \text{ recip.resist.} + \log \frac{d \text{ recip.resist.}}{dt} = \\ 1 \log (C_F - B \text{ recip.resist.}^A) + \\ m \log (\text{recip.resist.}^A \text{ end rapid reaction} - \text{recip.resist.}^A) \\ + \text{constant}_1 \end{aligned} \quad (75)$$

At constant chloramine concentration, additional simplification gives equation (76) which is the form tested in the plot of Figure 83.

$$\begin{aligned} (A-1) \log \text{ recip.resist.} + \log \frac{d \text{ recip.resist.}}{dt} = \\ m \log (\text{Recip.resist.}^A \text{ end rapid reaction} - \text{recip.resist.}^A) \\ + \text{constant}_2 \end{aligned} \quad (76)$$

Figure 83

Log of the Rate of Formation of Ammonium Chloride in the Region of Rapid Reaction at Constant Chloramine and Ammonium Chloride Concentrations, versus a Function of the Hydrazine Concentration at -75°C .

Log of the rate of formation of ammonium chloride in the region of rapid reaction at constant chloramine and ammonium chloride concentrations versus a function of the hydrazine concentration for several experiments in which hydrazine was initially added to a chloramine solution in liquid ammonia at -75°C .

Slopes were measured at 40×10^{-5} mhos for experiments done in cell 3 and at 37×10^{-5} mhos for experiments done in cell 4. These reciprocal resistances correspond to the same concentration of NH_4Cl in the respective cells.

The placement of the straight line was determined by the method of least squares.

Log of the rate of formation of ammonium chloride in the region of rapid reaction at constant ammonium chloride concentration vs. a function of the hydrazine concentration at -75°C

Fig.83

The data showed very little conformity to any pattern in the preliminary plot and only a poor conformity to a trend in the plot of Figure 83 used in testing equation (76). The straight line was laid by use of a least squares treatment. The order with respect to concentration of hydrazine appeared to be 1.2.

In addition to the plotted points showing very little conformity to any trend, the test of the kinetics was limited to the post break region of rapid reaction. The results were so indecisive that the use of this method was abandoned.

Calculations were made to test the free radical chain mechanism proposed in equations (60) - (72). The test was made by applying an expression for rates derived from the mechanism for that composition which corresponds with the point of inflection in the rate data. Under the assumption that the rate determining step involves the concentration of the chain carrier, $\text{NH}_2^\bullet$, the time rate of change of its concentration is expected to be zero at the inflection point, i.e., the concentration of the amide radical, $\text{NH}_2^\bullet$, would be passing through a maximum, $\frac{d [\text{NH}_2]}{dt} = 0$.

The expression for the rate of hydrazine formation at the inflection point, derived from the mechanism outlined in equations (60) - (72) is described on the nextpage.

$$\begin{aligned}
 - \frac{d [\text{N}_2\text{H}_4]}{dt} = & \left[\text{N}_2\text{H}_4 \right]_t k_{68} \left(\frac{k_{64} k_{60}}{k_{72} k_{58}} \right)^{1/2} \left\{ \left[\text{N}_2\text{H}_4 \right]_o \left[\text{NH}_2\text{Cl} \right]_o (1 - e^{-k_{58}t}) \right. \\
 & \left. + \frac{\left[\text{NH}_2\text{Cl} \right]_o^2}{2} (1 + e^{-2 k_{58}t} - 2 e^{-k_{58}t}) \right\}^{1/2} \quad (77)
 \end{aligned}$$

where the subscript, "t", refers to the time elapsed at the inflection point, and the subscript, "o", refers to the time at the beginning of the experiment.

The test of the expression lay in the reproducibility of the ratio of the terms on the right to the terms on the left in a number of independent experiments. The ratio should equal the ratio of constants

$$k_{68} \left(\frac{k_{64} k_{60}}{k_{72} k_{58}} \right)^{1/2} \quad \text{at the inflection point.}$$

The location of the inflection point was readily judged in those cases in which the decomposition reaction gradually merged with the formation reaction, giving a rounded portion of the curve at the break. Such was the case of most of the experiments in the first series which were used to test the equation. The experiments of the series were R5⁻⁷⁵ through R22⁻⁷⁵. In experiments in which the break occurred abruptly, the inflection point was judged to coincide with the point of the break.

This situation is illustrated in the second series, Experiments R30⁻⁵⁰ through R32⁻⁵⁰, R34⁻⁵⁰ and R35⁻⁵⁰.

A considerable expansion of equation (77) resulted when the concentrations were expressed in terms of the experimental data. In order to process the calculations associated with the twenty test cases listed above, a table of calculations was set up which was 20 rows deep and 65 columns wide. The first and last columns of this table are reproduced in Table 54.

The ratios are seen not to be constant. For the reasons explained on page 344 it is not surprising that they are not. However, in view of the large number of phenomena that the mechanism accounts for it is thought that the complications must result from partial heterogeneous and/or metal catalyzed initiation of the reaction. The mechanism is in general consistent with the stoichiometry, the period of induction, the relatively large reaction rate, the temperature insensitivity and the lack of randomization of isotopic nitrogen associated with the decomposition reaction.

Table 54. Ratio of Rate Constants of the Reactions in the Proposed Free Radical Chain Mechanism for the Decomposition Reaction.

Experiment number	Ratio of Rate Constants
	$k_{68} \left(\frac{k_{64} k_{60}}{k_{72} k_{58}} \right)^{1/2}$
R5-75	3.09
R6-75	44.9
R8-75	33.9
R9-75	5.23
R10-75	54.3
R12-75	4.18
R13-75	178.
R14-75	3.67
R15-75	
R16-75	7.98
R17-75	10.4
R18-75	14.0
R19-75	.470
R20-75	1.63
R22-75	12.3
R30-50	240.
R31-50	538.
R32-50	229.
R34-50	50.5
R35-50	436.

SUMMARY

In the synthesis of hydrazine from chloramine and ammonia in liquid ammonia solution two principal reactions are encountered. The first leads to the formation of hydrazine, the second, to its destruction. The study of the kinetics of these two reactions by a conductimetric method is the subject of this work.

The conductimetric method is possible due to the accumulation of the conducting product, ammonium chloride, formed in the course of both reactions.

By proper choice of experimental conditions it was found possible to isolate the hydrazine forming reaction and the hydrazine decomposing reaction and to subject them separately to kinetic investigation.

The rate of the hydrazine forming reaction,

was measured at -75° , -60° , -50° , and -38°C . The reaction was found to be first order with respect to chloramine, and its rate was independent of the ionic strength and acidity in solutions of ammonium chloride from 0.001 to 0.01 molar. From the temperature dependence of the rate constants, the Arrhenius energy of activation, 13.3 kcal. per mole, and the entropy of activation, -22.6 e. u. per mole, were obtained. The data suggest that the rate-determining

step in the formation of hydrazine is

The rate of the decomposition reaction,

was also followed conductimetrically at -75° , -60° , -50° , and -38°C . Its stoichiometry was measured by three independent methods. The overall decomposition reaction, equation (3), was found to have a much lower temperature coefficient than the formation reaction, equation (1). This factor favors higher yields of hydrazine at higher temperatures.

The decomposition reaction was found to exhibit an induction period which is sufficiently long to permit the formation reaction to give useful yields of hydrazine. The higher yields obtained in the more dilute solutions of chloramine are accounted for in part by the fact that the induction period is lengthened by decreasing the concentrations of chloramine and hydrazine.

A possible detailed free radical chain mechanism for the reactions summarized by equation (3) is considered. It involves the slow formation of the intermediate, triazane, possibly needed for chain initiation. The delay in accumulating triazane is suggested to account for the induction period. Triazane is thought to decompose to form the amide radical, $\text{NH}_2^\bullet$, which is

the chain carrier. The chain initiating step is thought to be homogeneous and/or surface and metal ion catalyzed. The latter two complications may account for erratic variations in length of the induction period. It is postulated that most of the hydrazine passes through the intermediate, diazene, $\text{HN}=\text{NH}$, in the chain process and only a small fraction is consumed in forming the chain initiator, triazane. This mechanism predicts almost no randomization of the atoms of nitrogen contained in the hydrazine during its oxidation by chloramine.

BIBLIOGRAPHY

- Audrieth, L. F., Colton, Ervin, and Jones, M. M., "Formation of Hydrazine from t-Butyl Hypochlorite and Ammonia," Journal of the American Chemical Society, Vol. 76 (March 5, 1954), pp. 1428-1431
- Audrieth, L. F., and Diamond, L. H., "Preparation of N-Substituted Hydrazine by Modification of the Raschig Synthesis," Journal of the American Chemical Society, Vol. 76 (Oct. 5, 1954), pp. 4869-4871.
- Audrieth, L. F., and Ogg, B. A., The Chemistry of Hydrazine. New York, John Wiley and Sons, Inc., 1951
- Bodenstein, Max, "Monochloramin und Hydrazin. II. Bildung von Hydrazin und Zersetzung von Monochloramin in ammoniakalischer Lösung," Zeitschrift für Physikalische Chemie, Vol. 139A (1928), pp. 397-415.
- Browne, A. W., "A New Synthesis of Hydronitric Acid," Journal of the American Chemical Society, Vol. 27 (May, 1905), pp. 551-555.
- Cahn, J. W., and Powell, R. E., "Oxidation of Hydrazine in Solution," Journal of the American Chemical Society, Vol. 76 (May 5, 1954), pp. 2568-2572.
- Cahn, J. W., and Powell, R. E., "The Raschig Synthesis of Hydrazine," Journal of the American Chemical Society, Vol. 76 (May 5, 1954), pp. 2565-2567.
- Clark, Charles G., Hydrazine. Baltimore, Md., Mathieson Chemical Corporation, 1953.
- Colton, Ervin, Jones, M. M., and Audrieth, L. F., "The Preparation of Hydrazine from Urea and t-Butyl Hypochlorite," Journal of the American Chemical Society, Vol. 76 (May 5, 1954), pp. 2572-2574.
- Cross, C. F., and Bevan, E. J., "The Interaction of Hypochlorites and Ammonium Salts. Ammonium Hypochlorite," Proceedings of the Chemical Society (London), Vol. 6 (Feb., 1890), pp. 22-24.

Curtius, Theodor, "Ueber das Diamid (Hydrazin)," Berichte der deutschen Chemischen Gesellschaft, Vol. 20 (1887), pp. 1632-1634.

Curtius, Theodor, and Jay, R., "Ueber das Hydrazin," Journal für Praktische Chemie, Vol. 39(2) (Jan., 1889), pp. 27-58.

Drago, R. S., and Sisler, H. H., "The Effect of Hydroxide and Ammonium Ions on the Reaction of Chloramine with Aqueous Ammonia," Journal of the American Chemical Society, Vol. 77 (June 20, 1955), pp. 3191-3194.

Fischer, Emil, "Ueber aromatische Hydrazin-verbindungen," Berichte der deutschen Chemischen Gesellschaft, Vol. 8 (1875), pp. 589-594.

Frost, A. A., and Pearson, R. G., Kinetics and Mechanism New York, John Wiley and Sons, Inc., 1953

Harned, H. S., and Owen, B. B., The Physical Chemistry of Electrolytic Solutions, 2nd ed. rev. New York, Reinhold Publishing Corporation, 1950.

Higginson, W. C. E., and Sutton, D., "The Oxidation of Hydrazine in Aqueous Solution. Part II. The Use of ^{15}N as a Tracer in the Oxidation of Hydrazine," Journal of the Chemical Society (London), Vol. 287 (1953), pp. 1402-1406.

Higginson, W. C. E., Sutton, D., and Wright, P., "The Oxidation of Hydrazine in Aqueous Solution. Part I. The Nature of 1- and 2-Electron-transfer Reactions, with Particular Reference to the Oxidation of Hydrazine," Journal of the Chemical Society (London), Vol. 282 (1953), pp. 1380-1386.

Hurley, Forrest Keyburn, "Studies in Nitrogen Chemistry." Ph.D. dissertation, The Ohio State University, 1954.

Jander, Jochen, "Ein Beitrag zur Kenntnis des Monochloramins," Die Naturwissenschaften, Vol. 42 (April, 1955), pp. 178-179.

Jander, Jochen, "Ueber Lösungen von Chloramin in flüssigem Ammoniak," Zeitschrift für anorganische und allgemeine Chemie, Vol. 280 (Sept., 1955) pp. 264-275.

- Jander, Jochen, "Zum Verstandnis der Chemie der Chlor-Stickstoff- und Chlor-Saurestoff-Verbindungen," Zeitschrift fur anorganische und allgemeine Chemie, Vol. 280 (Sept., 1955), pp. 276-283.
- Jolly, William L., "The Thermodynamic Properties of Chloramine, Di-Chloramine, and Nitrogen Tri-Chloride," Journal of Physical Chemistry, Vol. 60 (April, 1956), pp. 507-508.
- Jones, M. M., Audrieth, L. F., and Colton, Ervin, "Studies on the Raschig Synthesis of Hydrazine: The Reaction between Aqueous Chloramine and Ammonia Solutions," Journal of the American Chemical Society, Vol. 77 (May 20, 1955), pp. 2701-2703.
- Joyner, Reginald, A., "Preparation of Hydrazine by Raschig's Method," Journal of the Chemical Society (London), Vol. 123 (1923), pp. 1114-1121.
- Kirke, R. E., and Browne, A. W., "Oxidation of Hydrazine. VIII. Mono-Deelectronators and Di-Deelectronators," Journal of the American Chemical Society, Vol. 50 (Feb., 1928), pp. 337-347.
- Laitinen, H. A., "Lower Oxidation States in Liquid Ammonia," Final Report to the Office of Naval Research, Contract Norn. 21900NR052247.
- Mattair, Robert, and Sisler, H. H., "The Production of Hydrazine by the Reaction of Chlorine with Anhydrous Ammonia," Journal of the American Chemical Society, Vol. 73 (April 10, 1951), pp. 1619-1622.
- Omiotanski, George M., and Sisler, H. H., "The Reaction of Chloramine with Tertiary Amines. 1,1,1-Trisubstituted Hydrazinium Salts," Journal of the American Chemical Society, Vol. 78 (March 20, 1956), pp. 1211-1213.
- Raschig, F., Schwefel-und Stickstoffstudien. Leipzig-Berlin, Verlag Chemie, G.m.b.H., 1924.

- Sisler, H. H., Boatman, C. E., Neth, F. T., Smith, Robert, Shellman, R. W., and Kelmers, Donald, "The Chloramine-Ammonia Reaction in Pure Water and Other Solvents," Journal of the American Chemical Society, Vol. 76 (Aug. 5, 1954), pp. 3912-3914.
- Sisler, H. H., Neth, F. T., Drago, R. S., and Yaney, Doyal, "The Synthesis of Chloramine by the Ammonia-Chlorine Reaction in the Gas Phase," Journal of the American Chemical Society, Vol. 76 (Aug. 5, 1954), pp. 3906-3909.
- Sisler, H. H., Neth, F. T., and Hurley, F. R., "The Chloramine-Ammonia Reaction in Liquid Ammonia," Journal of the American Chemical Society, Vol. 76 (Aug. 5, 1954), pp. 3909-3911.
- Thiele, Johannes, "Notiz ueber die Einwirkung von Ammoniak auf Hypochlorite," Justus Liebigs Annalen der Chemie, Vol. 273 (1893), pp. 160-163.
- Wiberg, Egon, and Schmidt, Max, "Ueber den Reaktionsmechanismus der Raschigschen Hydrazinsynthese," Zeitschrift für Naturforschung, Vol. 66 (1951), p. 336.
- Zimmer, Hans, "Neuere Entwicklengen auf dem Gebiet der Hydrazinchemie," Chemiker Zeitung, Vol. 79 (Sept., 1955), pp. 599-605.

AUTOBIOGRAPHY

I, Francis Nash Collier, Jr., was born in New York, New York, February 11, 1917. I received my secondary education in the public schools of Birmingham, Alabama. My undergraduate training was obtained at Howard College, Birmingham, Alabama, from which I received the degree of Bachelor of Science with honors in chemistry in 1942. I then worked as a Junior Chemical Engineer in the Chemical Warfare Service Arsenal at Huntsville, Alabama. I returned to Howard College in 1943 to teach general physics and general chemistry.

In 1946 I entered the Graduate School of The Ohio State University and, working under the direction of Dr. H. E. Wirth, received my Master of Science degree in chemistry in 1949. While in residence at The Ohio State University I was employed as an assistant instructor in charge of the physical chemistry laboratories. In 1949 I returned to Howard College to teach physical chemistry.

In September, 1953, I received a research fellowship to work under the direction of Dr. H. H. Sisler on the chemistry of chloramine and hydrazine. I held this position for three years with the exception of a period of nine months during which I was appointed as duPont Teaching Fellow in the department of chemistry.

I was elected to associate membership in the Society

of the Sigma Xi in 1949 and to full membership in 1956.

In September of 1956 I returned to Howard College to become chairman of the department of physics. In June of 1957 I accepted a position in the department of chemistry at the University of North Carolina at Chapel Hill, N. C. in the division of inorganic chemistry.