more readily reproducible than when prepared with air-dried electrodes and solutions stirred either mechanically in the presence of air or with compressed air or oxygen.

2.   In the preparation of the quinhydrone half-cell it is not sufficient to dry the electrodes with nitrogen; nitrogen must be passed through the solution.   If, however, nitrogen is passed through the solution the electrodes need not be dried with nitrogen.

3.   The 0.1 N hydrochloric acid quinhydrone half-cell, prepared as described in this and in the first paper of this series, is the most easily and readily reproducible electrode which the authors have used.

4.   Electrodes prepared with nitrogen acquire a definite equilibrium potential much more quickly than those prepared with air.

5.   Short circuiting the electrodes in pairs during pre-treatment does not affect the potential differences obtained in nitrogen.

Work is in progress which involves an inter-comparison of the electrodes of different series made up of electrodes of different metals and of different sizes of the same metal.

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THE ATOMIC WEIGHTS OF NITROGEN AND SILVER. I.   THE RATIO OF AMMONIA TO SILVER

BY GREGORY PAUL BAXTER AND CHARLES HERBERT GREENE

Because accurate, simple and direct methods are lacking, until recently the atomic weight of nitrogen has been less certainly known than most of those of elements of low atomic weight.   But in view of recent gravimetric evidence, as well as gas density and mass spectrograph measurements, there now seems to be little doubt that the value of this constant is very nearly 14.008.

This paper describes an investigation of the ratio $Ag:NH_3$.   The ratio $NO_3:Ag$ is already known with a higher degree of precision than most gravimetric ratios.[1]   By combining the two the ratio $NH_3:NO_3$ may be obtained.   This with the assumption of the atomic weights of hydrogen and oxygen makes possible the calculation of the atomic weight of nitrogen. In spite of the fact that the method of calculating the atomic weight of nitrogen is indirect, the result is not particularly sensitive to experimental error, for an uncertainty in the ratio $NH_3:NO_3$ affects the atomic weight of nitrogen by a proportion only 60% greater, while a given uncertainty in

[1] 0.57479, Richards and Forbes, *Pub. Car. Inst.*, No. 69, 47 (1907); Hönigschmid, Zintl and Thilo, *Z. anorg. allgem. Chem.*, 165, 284 (1927).

the atomic weight of hydrogen affects the atomic weight of nitrogen in a proportion one-third as large.

The outline of the experimental procedure was as follows. Ammonia was weighed while adsorbed on dehydrated chabazite in a closed tube. A suitable quantity of the ammonia was then caused to evaporate into dilute hydrochloric or hydrobromic acid until the acid was exactly neutralized. The halogen content of the solution was then found by nephelometric comparison with the purest silver in the usual way.

The first step in the investigation was to make certain that the endpoint in the comparison of ammonia with hydrochloric and hydrobromic acids could be determined with the necessary degree of precision. We found that this could be accomplished by using either methyl red or litmus as indicator. Approximately one normal solution of ammonium chloride, which had been subjected to one, two, three and four crystallizations from conductivity water, gave the same tint with methyl red, as nearly as could be determined, provided the crystals had been centrifugally drained and thoroughly rinsed to remove the mother liquor. The mother liquor itself was always more acid owing to escape of ammonia formed by hydrolysis.

Furthermore, if the solutions of ammonium chloride were deliberately made slightly acid or basic by addition of small amounts of hydrochloric acid or ammonium hydroxide immediately before crystallization, the crystals, if thoroughly rinsed, gave solutions of the same acidity as those of salt which had been crystallized without such additions.

The color of the indicator in 100 cc. of a normal solution of the chloride was perceptibly altered by the addition of 0.1 ml. of 0.01 normal base or acid. Since this quantity of acid corresponds to only 0.001% of the salt present, it was evident that the comparison of ammonia with hydrochloric acid could be carried out with sufficient accuracy.

Although there seemed to be every reason to expect that ammonium bromide would behave in the same manner, similar experiments were made with carefully purified ammonium bromide, without disclosing any differences, except that corresponding solutions of the bromide seemed to produce a slightly pinker shade with methyl red.

Some of the later experiments were carried out with litmus instead of methyl red. In spite of the fact that the color change of the former indicator extends over a greater P_H range, the sensitiveness of the end-point was only slightly reduced.

Although the ratio of ammonia to silver found by comparing the halide solution with the silver solution is independent of the particular halogen involved, the hydrochloric and hydrobromic acids were carefully purified. Good quality hydrochloric acid was diluted with an equal volume of water, and after the addition of a small amount of potassium permanganate to liberate bromine and iodine if present, the nearly constant boiling solution

was distilled through a quartz condenser. The first half of the distillate was rejected as well as a small residue in the still. The portion retained was a second time distilled in the same way. The middle portion of the distillate was preserved in a quartz flask.

Hydrogen bromide was produced by synthesis from pure hydrogen and bromine, and the solution was further purified by distillation. Bromine was freed in large part from chlorine by solution in aqueous potassium bromide, and distillation. A portion of the partially purified bromine was converted into potassium bromide by addition to a solution of recrystallized potassium oxalate and the remainder of the bromine was subjected to a second distillation from solution in this bromide. All the product was next converted to potassium bromide by reaction with three times crystallized potassium oxalate, and after evaporation of the solution the residual potassium bromide was fused in a platinum dish with the addition of small amounts of potassium permanganate to oxidize organic matter. A concentrated solution of the bromide was boiled with a small amount of permanganate and sulfuric acid to remove residual iodine, and then the solution was cooled and treated with a considerable excess of sulfuric acid which had been heated to fuming to remove volatile acids. The potassium sulfate which deposited was separated and bromine was liberated from the solution by adding about 80% of the theoretical amount of permanganate. After distillation from the solution the bromine was washed with water and once distilled.

Hydrogen bromide was prepared by saturating pure electrolytic hydrogen with bromine at 44° and passing the mixture over hot platinized asbestos. Any excess of bromine was removed by washing the gas with ferrous bromide solution and the washed gas was then absorbed in the purest water. Two distillations of the resulting solution through a quartz condenser followed, only the middle portions of the constant boiling distillate being retained. The acid was preserved in a pyrex flask, and remained colorless.

Another specimen of hydrobromic acid was prepared by distilling a solution which resulted from work on nickelous bromide carried on by Professor S. Ishimaru.[2] The bromine used in this preparation had been subjected to the same treatment as ours. The acid seemed to have a slight tendency to decompose on standing.

Pure ammonia was prepared by fractional distillation of liquid ammonia in an all-glass apparatus constructed for the purpose by Dr. E. K. Haviland in connection with another research. The original material was commercial synthetic liquid ammonia supplied in a steel cylinder. McKelvey and Taylor[3] have shown that the important impurities in such material are

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[2] Baxter and Ishimaru, THIS JOURNAL, 51, 1729 (1929).

[3] McKelvey and Taylor, *Bur. Standards, Sci. Pub.* 365.

moisture and non-condensing gases. The cylinder A (Fig. 1) was connected by means of a copper tube B to the glass purifying apparatus by means of hard de Khotinsky cement. The mercury relief valve D was long enough to permit evacuation of the apparatus. After passing through the mercury bubbler E and the trap F the gas was passed over fused potassium hydroxide in the two towers C, and through the tube H filled with the dehydrated adsorbent gmelinite, both for the removal of water, and through the sintered glass dust filter H_1. The first portion of ammonia was condensed by chilling with ether–solid carbon dioxide in L. The
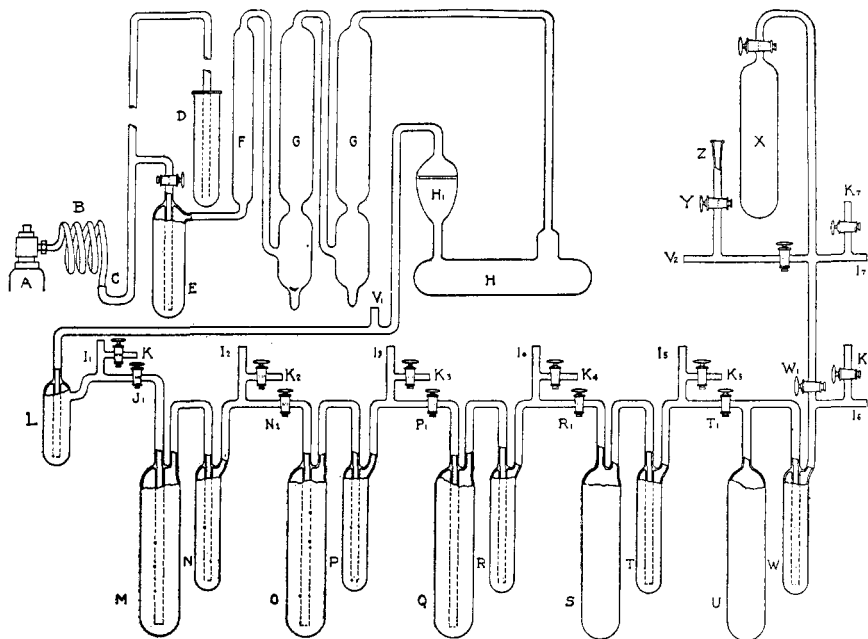

Fig. 1.—Ammonia purification train.

succeeding portions of gas were caused to bubble through the liquid ammonia in L before condensation in M. The material in L was then rejected by evaporation through the safety tube I, or through the line K, into a bottle containing dilute sulfuric acid. From M a light fraction was distilled into N which had previously been evacuated, and the remainder of the ammonia in M was condensed in O after bubbling through the liquid in N. A third similar distillation from O to Q followed. A large proportion of non-condensing gaseous impurities must have been eliminated in the three distillations. The removal of the remainder was secured by the method used by McKelvey and Taylor of condensing the ammonia as a solid by chilling S with liquid air. Uncondensed gases were then removed by exhausting S. Two more similar distillations from S to U, and from U

to X followed.   In each of these distillations a light and a heavy fraction were rejected.   The purified ammonia was stored in X at room temperature under pressure.

The silver used in the comparison with the ammonium halide was purified by standard methods by Dr. William C. Cooper for the analysis of germanium halides.[4]

The ammonia was weighed in a tube containing dehydrated chabazite (Fig. 2), provided with a well ground stopcock lubricated with rubber grease, and a sintered glass dust filter to prevent loss of chabaz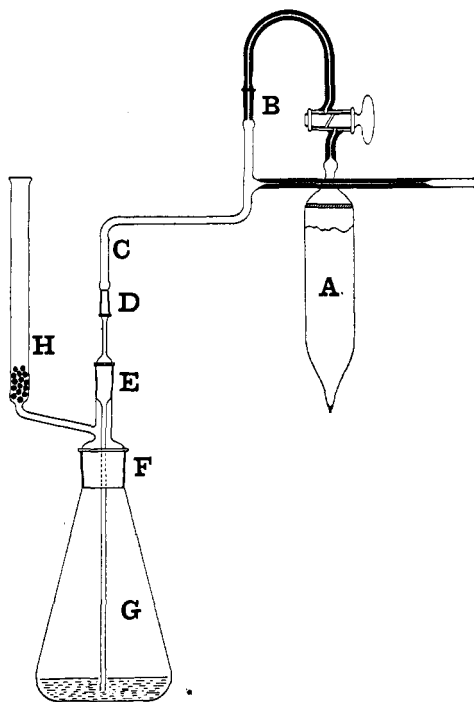ite powder during the expulsion of the ammonia.   This chabazite had been previously employed in other experiments on adsorption.   Before use in the ammonia tube it was heated to 575° in a high vacuum to eliminate so far as possible residual water and other gases to which it had previously been exposed. In the course of our experiments it was many times saturated with pure ammonia and the ammonia expelled by heating. This treatment undoubtedly removed any important amount of other gases which might not have been expelled in the initial treatment.   The experiments described below to determine whether the purified ammonia still contained moisture would not have differentiated between water contained in the ammonia and that given off by the chabazite during the expulsion of the ammonia.

Fig. 2.

The determination of the apparently very small water content of the ammonia was a far from simple task.   The method followed was to pass the ammonia expelled from the chabazite tube through a weighed tube containing freshly fused potassium hydroxide.   Baxter and Starkweather[5] have found the efficiency of this substance as a drying agent to be very high, for a liter of air dried with freshly fused hydroxide even at 50° con-

[4] Baxter and Cooper, *Proc. Am. Acad.*, 59, 236 (1924); 60, 220 (1925); *J. Phys. Chem.*, 28, 1049 (1924); 29, 1364 (1925).

[5] Baxter and Starkweather, THIS JOURNAL, 38, 2038 (1916).

tains only 0.006 mg. of water, while at 25° the residual amount of water per liter can hardly exceed 0.002 mg.   In spite of the fact that McKelvey and Taylor reject this method of determining moisture in ammonia as unreliable, we feel that it is fully as satisfactory as the one advocated by them of evolving acetylene from calcium carbide.   Possibly the difficulty experienced by them with potassium hydroxide may have come from incomplete dehydration of the hydroxide at the start.

Since preliminary experiments in which rubber connections were included in the apparatus exhibited irregularities which disappeared when rubber was eliminated, the final apparatus had only sealed or ground connections. The results of the experiments in which rubber was used were not on the whole different from those with the final improved apparatus.

The procedure in the moisture determinations was as follows.   A glass-stoppered U-tube containing potassium hydroxide was provided with a ground joint and a counterpoise of similar construction, volume and weight, but containing no caustic.   After being wiped with first a damp and then a dry cloth, both the adsorption tube and the counterpoise were hung on a balance and left for several hours.   One stopcock on each was then carefully opened and after about an hour the differences in weight were determined.   The average difference between duplicate weighings was 0.014 mg. and the algebraic sum of fifteen such differences was 0.01 mg. In order to prevent diffusion of moisture into the potassium hydroxide tube while open to the air, the orifice of the outlet tube was constricted to a fine capillary.   Even this did not prevent a slow but steady gain of 0.01 mg. per hour; therefore, a correction of this magnitude was applied for the period during which the tube remained open.

Both the chabazite tube containing ammonia and the absorption tube in that order were connected by greased ground joints to a line through which was flowing air which had been finally dried by means of fused potassium hydroxide.

The stopcocks of the absorption tube were then opened and ammonia was expelled from the chabazite tube through the absorption tube.   Finally the chabazite tube was closed and the ammonia swept out of the absorption tube with the air current.   Twelve similar runs in which no ammonia was involved yielded only 0.29 mg. of water in all.   An average correction of -0.024 mg. was therefore applied in each experiment with ammonia.   The results of the three final experiments with ammonia are given in the following table.

Wt. of NH_3	Wt. of H_2O	Wt. of H_2O corrected for blank	Per cent. of H_2O
3.14	0.00014	0.00012	0.0038
4.66	.00009	.00007	.0015
2.27	.00013	.00011	.0048
Total 10.07	.00036	.00030	.0030

Another experiment with 1.42 g. of the residual liquid ammonia from a fractional distillation yielded 0.0056% of moisture.

McKelvey and Taylor[3] state that the most nearly anhydrous ammonia prepared by them contained 0.004%. At any rate it seems unlikely that any appreciable amount of water was introduced from the chabazite itself.

The quantitative comparison of ammonia with silver was conducted in the following manner. The chabazite tube charged with ammonia was carefully compared with a similar sealed counterpoise of similar exterior volume by suspending them on opposite arms of a balance in a balance room kept thermostatted within a degree or two to prevent alteration in the ratio of the lengths of balance arms. By means of the greased ground joint B (Fig. 2) the chabazite tube was connected with the tube C delivering into the Erlenmeyer flask G which contained the acid (1 normal, containing indicator) to be neutralized. Just before use this acid was further twice freshly distilled through a quartz condenser, only the middle portion being retained. The tube C delivering into the Erlenmeyer flask was connected with a supply of the purest electrolytic hydrogen. The ground joints E and F were wet with water and the guard tube H containing a few glass pearls was wet with tenth normal acid. The ground joint D was lubricated with grease.

After the apparatus had been filled with hydrogen, the chabazite tube was warmed gently with an electric oven and ammonia was allowed to flow into the hydrogen stream, except in Analysis I when the hydrogen was shut off. It was possible to determine very closely when the acid was neutralized and as soon as the end-point was nearly reached the stopcock of the chabazite tube was closed and the ammonia in the connecting tubes was swept into the flask by passing the hydrogen current for some time. The guard tube was then rinsed into the flask.

The chabazite tube was next disconnected, the ground joint cleaned with ether, and the tube again compared with the counterpoise by adding weights to the side of the balance on which the tube was hung, so that the ammonia was weighed by substitution.

To find the exact neutral point all parts of the stopper and tubes were rinsed with freshly distilled and boiled water and then the ammonium halide solution was brought to the desired shade by adding hundredth normal acid and barium hydroxide. The barium hydroxide solution had been analyzed by exactly neutralizing with hydrobromic acid and precipitating silver bromide.

In the first five experiments the standard color was produced in an acetate buffer solution which had been brought to the same shade as that given by a solution of the ammonium halide (normal). In the later experiments the standard color produced by a solution of carefully recrystallized ammonium halide was used. In Experiments 1, 2, 3, 5 and 6 methyl red

dissolved in redistilled alcohol was employed, while in Experiments 10, 12, 14 and 16 a saturated aqueous solution of methyl red was substituted. For Experiments 7, 9 and 11, litmus was prepared by extracting commercial powder with hot alcohol, dissolving in water, precipitating with alcohol and dissolving in water for use. None of the indicator solutions used gave any precipitate with silver nitrate. As nearly as possible the same amount of indicator was added to the solution being titrated and to the standard color solution, and the volumes and concentrations of both were made very closely the same.

After the neutralization was complete the solution of the ammonium halide was transferred to the precipitating vessel, a 3-liter Erlenmeyer flask with a carefully ground stopper or an 8-liter bottle, and diluted. A very nearly equivalent amount of the purest silver was carefully weighed by substitution and dissolved in chlorine-free nitric acid, with especial precautions to avoid loss of spray. This solution of silver was diluted to approximately the same volume as the halide solution and then added in small portions with gentle agitation to the halide solution. The exact end-point was then found with the use of a nephelometer, by testing the supernatant liquid occasionally with equivalent amounts of halide and silver, and making up a deficiency of either by means of hundredth normal halide and silver solutions. This process always was continued for a month or more in order to allow salts occluded by the silver halide to be leached out so far as possible.

The weight of silver actually equivalent to the ammonia was found by subtracting the silver equivalent of the barium hydroxide used in the neutralizing and adding the net amount of silver used in the halide–silver comparison.

The loss in weight of the ammonia tube was corrected for buoyancy of the air on the weights and the weight of silver for buoyancy of the air on both silver and weights. For this purpose the density of the weights was assumed to be 8.3 and that of silver 10.49. The density of the air was calculated from the conditions at the time of each weighing.

In the following table the weights of ammonia are corrected for moisture content by subtracting 0.003% (page 609). The ratio $NO_3:NH_3$ is calculated assuming $NO_3/Ag = 0.57479$.[1]

After the earlier experiments in the above table had been completed (Analyses 1 to 7), it was evident that the ratio of silver to ammonia was lower when hydrobromic acid was used for neutralization than when hydrochloric acid was used. A search for the cause of this difference revealed the fact that in the case of hydrobromic acid the more concentrated the solutions during the precipitation, the lower the ratio. Since the silver solution was poured into the bromide solution in these experiments, a possible cause of the difficulty apparently lay in occlusion of soluble bromide by the silver bromide. To test this hypothesis in the following

TABLE I

THE ATOMIC WEIGHT OF NITROGEN

Ag = 107.880   H = 1.0078

Analysis	Concn., norm.	Acid neutr.	Indicator	Corr. wt. of NH₃ in vacuum	Wt. of Ag in vacuum	Corr. for Ba(OH)₂	Ag added or subtr.	Corr. wt. of Ag in vacuum	Ratio Ag:NH₃	Ratio NO₃:NH₃	At. wt. of nitrogen
1	0.09	HCl	M. R.	1.43953	9.11802	0.00000	+0.00065	9.11867	6.33448	3.64100	14.0067
2	.07	HBr	M. R.	4.67035	29.58363	.00000	− .00068	29.58295	6.33420	3.64083	14.0078
3	.06	HCl	M. R.	4.11520	26.06724	.00000	+ .00020	26.06744	6.33443	3.64097	14.0069
4	.08	HBr	M. R.	1.62620	10.30093	.00000	− .00079	10.30014	6.33387	3.64065	14.0090
5	.15	HBr	M. R.	1.85833	11.77136	.00000	− .00132	11.77004	6.33367	3.64053	14.0098
6	.09	HBr	L	1.81372	11.48867	− .00025	− .00038	11.48804	6.33397	3.64070	14.0087
7	.08	HCl	L	1.61251	10.21437	.00000	− .00040	10.21397	6.33421	3.64084	14.0078
8	.03	HBr	M. R.	1.92927	12.22401	− .00324	− .00040	12.22037	6.33419	3.64083	14.0078
9	.02	HCl	L	1.20999	7.66447	.00000	− .00021	7.66426	6.33415	3.64081	14.0080
10	.025	HBr	M. R.	1.67684	10.62236	− .00059	− .00019	10.62158	6.33428	3.64088	14.0075
11	.03	HBr	M. R.	1.8₍ ₎41	12.02690	− .00162	+ .00564	12.03092	6.33403	3.64074	14.0084
12	.03	HBr	M. R.	1.9₍ ₎₍ ₎7	12.59673	.00000	− .00080	12.59593	6.33385	3.64063	14.0091

Average of chlorides (1, 3, 7, 9)	6.33432	3.64090	14.0074
Average of concentrated bromides (2, 4, 5, 6)	6.33393	3.64068	14.0088
Average of dilute bromides (8, 10, 11, 12)	6.33409	3.64077	14.0082
Average of analyses 1, 3, 7, 8, 9, 10, 11, 12	6.33420	3.64083	14.0078

experiments with hydrobromic acid (Analyses 8, 10, 11, 12) the concentration of the solutions during precipitation was made from one-half to one-third that previously used. These experiments yielded results concordant with those of the earlier chlorides as well as with Experiment 9 in which the chloride solution also was made more dilute before precipitation. In Analyses 10 and 12 the bromide solution was added to the silver solution.

If the correction for water in the ammonia is omitted the ratios $Ag:NH_3$ and $NO_3:NH_3$ become 6.33401 and 3.64073, respectively, and the atomic weight of nitrogen 14.0085.

This investigation was interrupted before it was completed. It is unfortunate that a larger number of experiments could not have been carried out. The purity of the ammonia needs further investigation, especially as regards water, although the synthetic material which we used as the starting point is unlikely to be seriously contaminated with any impurities except permanent gases and moisture. On the whole the final outcome may be looked upon as valuable corroborative evidence that the atomic weight of nitrogen is very close to 14.008. The uncertainty of the method is apparently less than 0.001 unit, which compares very favorably with that of all other methods at present available for the purpose.

If nitrogen is taken as 14.0078, the atomic weight of silver may be calculated to be 107.879, while the value for nitrogen of 14.008 gives 107.880 from the $Ag:NH_3$ ratio and 107.879 from the $Ag:NO_3$ ratio.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

KINETICS OF THE POLYMERIZATION OF ETHYLENE AT PRESSURES ABOVE ONE ATMOSPHERE[1]

BY ROBERT N. PEASE[2]

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Previous work[3] has indicated that the only important primary reaction of ethylene when heated in glass to 400–600° at 1 atmosphere initial pressure is one of polymerization to higher mono-olefins (C_nH_{2n}). The point has not been conclusively demonstrated, however, as would be done if a considerable portion of the ethylene could be caused to polymerize without

[3] Day, Am. Chem. J., 8, 153 (1886); Bone and Coward, J. Chem. Soc., 93, 1197 (1908); Hague and Wheeler, ibid., 390–391 (1929); Pease, THIS JOURNAL, 52, 1158 (1930); Wheeler and Wood, J. Chem. Soc., 1823 (1930).