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Summary

It was found impracticable to determine accurately the solubility of tetranitro-aniline in the various solvents at room temperature or higher temperatures because of the tendency of the solute to decompose while in solution, so determinations were made at 0.0° except with benzene with which solubility was determined at the freezing point of 3.9°.

The solubility of tetranitro-aniline in these solvents is slightly lower than that of tetryl under the same conditions.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

A PRECISION MEASUREMENT OF THE COMPOSITION OF THE CONSTANT-BOILING MIXTURE OF HYDROGEN CHLORIDE AND WATER

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This paper offers a series of precision measurements of the composition of the constant-boiling mixture of hydrogen chloride and water as it is prepared for use in acidimetry. It is one of a series from the Ohio State Laboratory in which atomic-weight methods have been employed in studying substances used as standards in chemical measurements.

The importance of this constant-boiling mixture in volumetric analysis is sufficient warrant for such a precision study, but in addition there is the gratification of scientific curiosity as to whether the peculiar balance of physical conditions which arises in the distillation of the acid and water will produce a mixture which in definiteness of composition approaches a true chemical compound.

Historical

The existence of a constant-boiling mixture of hydrogen chloride and water has been known since the days of Dalton. Bineau¹ and Roscoe and Dittmar² published papers on it but Hulett and Bonner³ were the first to suggest its use as a standard in volumetric analysis and to offer determinations of its composition that could be accepted by analytical chemists. The following quotation describes their procedure for obtaining a mixture of constant composition. "By starting with hydrochloric acid about $d. = 1.10$, made up with an ordinary hydrometer or sp. gr. balance, and distilling off $\frac{3}{4}$ of the liquid taken, the following distillate should not differ by more than one part in 10,000 from the

¹ Bineau, *Ann. chim. phys.*, [3] **7**, 257 (1843).

² Roscoe and Dittmar, *J. Chem. Soc.*, **12**, 136 (1860).

³ Hulett and Bonner, *THIS JOURNAL*, **31**, 390 (1909).

figures given in the following table. This constant-boiling acid is not hygroscopic or noticeably volatile and may be easily weighed in a little flask."

The table referred to in this quotation was compiled by Hulett and Bonner from their own results and those of Roscoe and Dittmar. It gives the composition of the constant-boiling mixture as 20.242% of hydrogen chloride at 760 mm. pressure. For other pressures from 770 to 730 mm. 0.0024 is to be subtracted from this value for each millimeter above 760 and added for each one below 760. The air weight of mixture that contains 1 mole of hydrogen chloride is given for each 10 mm. interval of pressure. Other important data in this paper are (1) the density at 25°, 1.0962, of the constant-boiling mixture distilled at 760 mm. and (2) the boiling point 108.54°, at 763 mm.

A critical reading of Hulett and Bonner's excellent paper shows that their work should be considered as preliminary rather than final. The most important result, the composition of the mixture, rests upon only 3 pairs of silver chloride precipitations made in volume-measured aliquot parts of 3 weighed portions of as many distillates. The silver chloride was collected and weighed in a Gooch crucible but no further detail is given excepting that "the usual precautions" were taken.

Two other papers have been found containing carefully conducted series of analyses of this constant-boiling mixture prepared according to the method of Hulett and Bonner. Morey⁴ while studying benzoic acid as a standard in acidimetry prepared and analyzed such a mixture by the silver chloride precipitation method and Hendrixson⁵ in his investigation of the acid phthalates as standard substances made a Hulett and Bonner mixture and also analyzed it by silver chloride precipitation.

Data for the variation of the composition of the constant-boiling mixture with changes in pressure rest upon the work of Roscoe and Dittmar cited above. They obtained constant-boiling distillates at pressures from 65 to 2510 mm. and showed that the percentage of hydrogen chloride slowly increases as the pressure decreases. It is fortunate that the correction for pressure is so small, since otherwise the work of Roscoe and Dittmar could scarcely be used. Their pressures varied nearly 5 mm. during a distillation and at best they have but two experimental results at atmospheric pressure. These are 765 and 768 mm., too close together to have any value in calculating changes in composition. The nearest pressure they studied below that of the atmosphere is 630 mm., and the nearest one above is 960 mm. However, the curve drawn through all their points is smooth and the pressure-composition correction, therefore, is probably but little in error. Hulett and Bonner's set of determinations was made at pressures from 755 to 762 mm. but this difference was not significant in their silver chloride results though it showed in their accurate density determinations.

Confirmatory data for the effect of changes in pressure can be obtained from the work of Morey and Hendrixson. Morey's distillates were prepared at 755.5 mm. and Hendrixson's at 740 mm. This is a difference of 15.5 mm. and calculation shows that the corresponding difference in composition agrees with that given by Hulett and Bonner.

⁴ Morey, *THIS JOURNAL*, **34**, 1027 (1912).

⁵ Hendrixson, *ibid.*, **37**, 2352 (1915).

It cannot be said, however, that the variation of the composition of the mixture with the pressure has been determined with the accuracy demanded by its importance and consequently its redetermination will probably soon be undertaken in the Ohio Laboratory.

Experimental Work of this Paper

Preparation of Materials

Water.—Conductivity water was used in all cases.

Hydrochloric Acid.—"Strictly c. p." acid was diluted to a density of about 1.10 and 600cc. portions were distilled from a 1000cc. Richards⁶ flask. A Jena glass tube surrounded by a water jacket served as condenser. The first 20 cc. was discarded and the next 500 cc. was used for the final distillation for obtaining the constant-boiling distillates and residues. Samples B, C and D were prepared in this way. Samples E, F, G and H were prepared by passing purified hydrogen chloride into conductivity water. The gas was generated by bringing together conc. hydrochloric and sulfuric acids and, in order to make it comparable with hydrogen chloride as it is usually treated in precise work, the gas was passed through towers of beads moistened with sulfuric acid and was finally cooled in calcium chloride and ice, excepting Samples G and H which were cooled in solid carbon dioxide and ether.

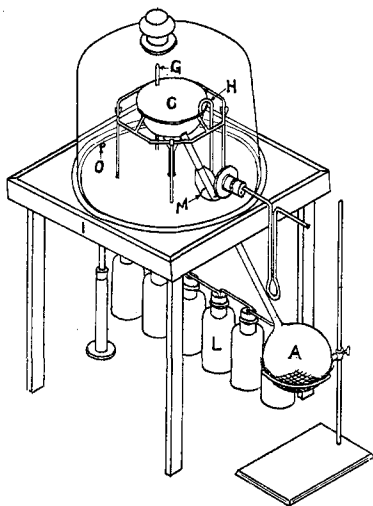


Fig. 1.

and is conveyed to any suitable receiving vessel under the apparatus. The cooling of the dish is accomplished by running water into it through the tube G and sucking it out through H. The base I which carries the bell jar and the supports for the dish is a wooden tray filled with ceresin obtained by melting hydrofluoric acid bottles. By warming the bell jar before putting it into position a tight joint is made around its bottom. To prevent the melting of this ceresin base at the place through which the neck of the boiling flask passes, a larger glass tube M is inserted first and the neck of the flask passed through it. A tight connection is made at the lower end of M by means of a stopper; the upper end is merely contracted a little. During a distillation a current of air purified by passing through the wash bottles L, is led into the bell jar through a hole in the stopper in M. This air passing through M keeps the space around the neck of the distilling flask cool. The flow of the air was regulated so that it replaced that carried out by the

⁶ Richards, *Proc. Am. Acad. Arts Sci.*, **30**, 380 (1894).

⁷ Morse and Burton, *Am. Chem. J.*, **10**, 311 (1888).

suction on the tube H. An opening at O in the ceresin base provided for the removal of any liquid that condensed on the bell jar. The platinum dish of our apparatus held 500 cc. and was cooled with tap water.

Silver Nitrate.—The silver nitrate was recrystallized 5 times from dil. nitric acid solution in platinum with centrifugal drainage between crystallizations. In order to avoid contamination by dust and fumes in the laboratory, these crystallizations were made in a special box equipped with a glass top and windows at the back. Holes provided with rubber sleeves admitted the arms of the experimenter. The sleeves were fitted with elastic bands which insured a suitable joint with the forearms while work was done in the box; at other times they were closed with clamps. As a further precaution against the entry of fumes, especially during such times as the vessels in the box were open, a current of purified air was forced in and allowed to escape through such places as were not air-tight. In this way a slight excess pressure was maintained on the inside of the box and the leaks were, therefore, all outward. The air was passed through sulfuric acid, potassium hydroxide solution, silver nitrate solution, Nessler's reagent and finally through a long tube full of cotton wool. As a further precaution against dust sev-

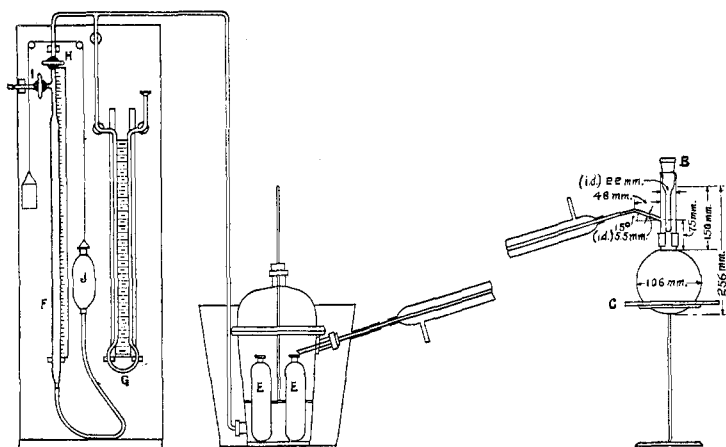


Fig. 2.

eral sheets of sticky fly paper were tacked on the inside walls. The heating of solutions in the box was done on an electric hot plate. The whole contrivance served its purpose admirably. Without it, it would have been impossible in our Laboratory to have worked in any precise way with silver salts and solutions.

Sodium Chloride.—One of the analyzed brands was reprecipitated thrice by hydrogen chloride and finally fused. Standard solutions were prepared from weighed portions.

Balance Weights and Weighing.—A long-arm Troemmer balance and carefully calibrated weights were used. The usual precautions in weighing were observed, even to taking into account the difference in density between the brass and fractional weights in applying the corrections for buoyancy. The weight of the same object taken at different times seldom varied more than 0.02 mg.

Barometer.—The barometer used was of the Fortin type and was compared with those at the United States Weather Bureau at Columbus. In determining the absolute pressures at which our distillations were made all of the known corrections were applied.

Distillation of Constant-boiling Mixtures.—The apparatus for obtaining the final constant-boiling distillates and residues is shown in Fig. 2.

The distilling flask held 635 cc. when filled to the neck. It was closed with the stopper B, shaped as shown and ground to fit tightly. The lower part of this stopper was of very thin glass designed to hold the thermo-element employed in testing the constancy of boiling point.⁸ The flask rested in an opening in the asbestos sheet C. This permitted the flame to touch the bottom of the flask but not its sides. Above the asbestos board, flask and neck were thickly covered with asbestos fiber cemented together with water glass. Seven g. of scrap platinum served to prevent bumping. Connection with the 75cm. condenser was made by a ground joint. The temperature of the tap water used for condensing varied from 20° to 30°. A Brühl jar carrying 5 special tubes, E, served for receiving the distillates. All stoppers used in this jar were paraffined corks. The whole receiving apparatus stood in a metal vessel and during a distillation was surrounded with ice. As soon as a distillation was finished the contents of the receivers and the residue in the distillation flask were transferred to glass-stoppered bottles which had been steamed for 30 minutes.

The pressure within the distillation apparatus was controlled in the following way. To increase it the cock H was opened and the water bulb J raised until the water manometer G registered as desired. In case J reached its upper limit before the pressure was high enough the cock H was closed, the one at I opened and J was lowered. This filled the tube F with air which could then be transferred to the apparatus by closing I, opening H and raising J. Reversing these operations reduced the pressure. All distillations were carried out under an absolute pressure of 750 mm. of mercury. This pressure inside the apparatus was obtained by putting in or taking out air until the readings on the water manometer combined with those of the barometer gave the desired value. The variations of pressure during a distillation were never more than 0.2 mm. of mercury.

The distillations were carried out by first filling the flask with 500 cc. of the prepared acid solution as described above. This was always about 1.1 in density. Five portions of distillate were always collected and the fifth or last one used for the analysis. The residual acid in the flask was also analyzed.

Analysis of Constant-boiling Mixtures.—The general scheme of analysis was to determine the chlorine in a weighed sample of distillate or

⁸ As a preliminary to a possible future study of the constant-boiling mixture as a means for obtaining a fixed point in thermometry, thermocouple readings were taken during a number of distillations with the view of noting the constancy of the boiling point of the mixture. Our equipment was designed to show fluctuations of temperature only, and it may be recorded here that the potentiometer readings indicated that the boiling point of the acid mixture did not vary more than 0.003° after equilibrium had been reached.

residual acid by precipitation with silver nitrate. The dried silver chloride was weighed first in a Gooch-Munroe crucible, and was then transferred to a porcelain crucible and fused. The loss on fusion gave the amount of water in the dried precipitate. Silver chloride in the wash and transfer waters was determined by the nephelometer, and that in the filtrate was estimated as 0.00003 g. per liter.⁹

In precipitating, filtering, washing, drying and fusing the silver chloride the Harvard methods were faithfully followed.

Eight portions of distillates representing 7 distillations and 4 portions of residues representing 3 distillations were analyzed. The final values calculated as percentage of hydrogen chloride, together with the necessary original data, are given in Table I. The chronological sequence of the distillations is indicated by the letters A, B, etc. The results are arranged in groups according to the rate of distillation. Abbreviations "dist." and "res." mean distillate and the corresponding residual acid left in the flask. The rate of distillation given is that of the mixture from which the actual portion analyzed was taken. Calculations are based on the atomic weights Ag = 107.88; Cl = 35.46; H = 1.008.

TABLE I
ANALYTICAL RESULTS

Distillation	Vol. of distillate Cc.	Vol. of residue Cc.	Rate of distillation Cc. per min.	Wt. of const.-boiling mixt. G.	Wt. of AgCl corres. to sample G.	HCl in mixture. %	Average of group dist. at same rate %
1 B(dist.)				9.13337	7.27249	20.260	20.261
2 B(dist.)	36	60	2.3	7.27251	5.79215	20.263	
3 B(res.)				8.26377	6.58087	20.260	
4 B(res.)				9.01746	7.18040	20.260	20.247
5 C(dist.)	51	42	3.0	7.08781	5.64142	20.249	
6 C(res.)				6.73759	5.36169	20.246	
7 D(dist.)	56	8	3.0	7.65972	6.09618	20.248	20.243
8 D(res.)				8.35008	6.57162	20.023 ^a	
9 H(dist.)	50	60	3.9	5.91192	4.70389	20.243	
10 F(dist.)	58	53	4.1	6.39525	5.08863	20.244	20.243
11 E(dist.)	54	34	4.2	7.48770	5.95826	20.245	
12 G(dist.)	52	51	4.3	6.44986	5.13108	20.240	

^a This value is not included in the averages because the solution was boiled so long that only 8 cc. remained in the distilling flask.

Discussion of Results

Effect of Rate of Distillation.—The results show that the percentage of hydrogen chloride in the constant-boiling mixtures diminishes as the rate of distillation increases. The effect is small and could be shown only by a series of precision measurements. Hulett and Bonner observed that evaporation on a water-bath or boiling in an open beaker gave mixtures

⁹ Richards and Wells, *THIS JOURNAL*, 27, 486 (1905).

that contained more hydrogen chloride than the distillates obtained when the flask is connected to a condenser in the ordinary way, and explained it by saying that it is "probably due to the fact that air had access to the surface of the evaporating liquid producing the same effect as distilling under diminished pressure." It is possible that in our distillations there was more air in the flasks when the boiling was moderate than when it was more rapid as in the case of the higher rates of distillation.

The effect was not noted until the work was finished, and consequently still higher rates of distillation were not tried to determine the point at which constancy of composition would be reached. We believe, however, that constancy of composition had been reached in the higher rates. A comparison of the averages of the three groups as given in the last column of Table I seems to show this. As a further note it should be recorded that with a flask of the size used the boiling was very violent at the higher rates.

Accuracy of Results.—The results as a whole cannot be compared among themselves on account of the effect of rate of distillation. If however they are grouped so that those corresponding to the same rates of distillation fall together, it will be seen that the maximum difference within a group is 5 in 20,000. This occurs in the third group.

Comparison of Distillates with Residues.—The results contain analyses of 3 residues left in the distilling flask after the constant-boiling distillate had passed over. These are shown in Nos. 3, 4 and 6. In all cases excepting the one noted in the table the composition of this residual acid agreed with that of its corresponding distillate.

Choice of the Most Probable Value.—Until a more extended study of the effect of rate of distillation on the composition of the constant-boiling mixture can be made it seems justifiable to reject all of the values of the first group in which the rate was low, and take the average of the other groups. Our choice of the most probable value may then be stated as follows: if the distillation is made at a pressure of 750 mm. of mercury, from a flask such as is described above and at the rate of 3 to 4 cc. a minute, the constant-boiling mixture contains 20.245% of hydrogen chloride. This is the average of the 7 experiments, 5 to 12 inclusive, omitting No. 8.

Comparison with Previous Work.—A direct comparison with previous results cannot be made because the conditions of analysis are not the same. Hulett and Bonner apparently made none of the usual corrections employed in precise work, and Morey and Hendrixson made only one, that for silver chloride dissolved in the washings. The corrections that should be used to bring the various series of results to a common basis make such an interesting exhibit in analytical chemistry that they are repeated here.

Vacuum weight of mixture is 100.091% of air weight; vacuum weight of silver chloride is 100.007% of air weight; silver chloride in washings

averaged 0.061% of weight of precipitate; water lost by fusing silver chloride averaged 0.014% of weight of precipitate.

Failure to apply the correction to vacuum in weighing the sample and the correction for water in the silver chloride causes the result to fall high and leaving off the other corrections causes a too low result. The net effect of using air weights throughout, not measuring the silver chloride in the washings and not fusing the silver chloride is +0.037%, that is, the result is 0.037% of itself too high.

By assuming that Hulett and Bonner made no corrections and that Morey and Hendrixson made none but the one noted above, and by assuming further that the corrections employed by us may be applied to their results, all of the values can be calculated to a common basis. Since these assumptions are reasonable, the calculation has been made. The four corrected results in terms of the percentage of hydrogen chloride in the constant-boiling mixture distilled at 750 mm. pressure are as follows: Hulett and Bonner, 20.258%; Morey, 20.252%; Hendrixson, 20.253%; and Foulk and Hollingsworth, (rapid distillation), 20.245% of hydrogen chloride.

The agreement among these 4 independent sets of results is remarkable and should tend to place this constant-boiling mixture on a firm basis as an analytical standard.

It is perhaps worth stating here that the average of our 4 results obtained on mixtures distilled at the slower rates is 20.261 and that the average of all of our results is 20.251% of hydrogen chloride. Either of these results agrees better with those of the other investigations than does the one selected but, nevertheless, we believe, for the present at least, that 20.245% is more nearly correct.

How to Use the Results.—In presenting the final results in a convenient form for the use of chemists one cannot do better than construct a table like that given by Hulett and Bonner.

TABLE II
USEFUL DATA FOR PREPARING STANDARD ACID SOLUTIONS

Pressure Mm. Hg	HCl Vacuum weight basis %	Air-weight of const.- boiling dist. that contains 1 mole, vac. Wt. of HCl G.
770	20.197	180.407
760	20.221	180.193
750	20.245	179.979
740	20.269	179.766
730	20.293	179.555

For the preparation of a standard acid a mixture of approximately 1.1 density should be distilled at the rate of 3 to 4 cc. a minute. After $\frac{3}{4}$ of the liquid has distilled the portion to be used as constant-boiling mixture

should be collected. Distillation must, however, not be pushed so far that less than 50 to 60 cc. of liquid remains in the flask. Reference to the table above and to the height of the barometer during the distillation shows the air weight of the constant-boiling mixture that contains 36.47 g. absolute or vacuum weight, of acid.

Summary

A set of precision measurements of the composition of the constant-boiling mixture of hydrogen chloride and water is given which shows the percentage of hydrogen chloride to be 20.245 if distillation is made at 750 mm. pressure.

It is shown that the rate of distillation affects the composition to a small extent.

Comparison is made with the results published in three other papers.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A REVISION OF THE ATOMIC WEIGHT OF TITANIUM. PRELIMINARY PAPER. THE ANALYSIS OF TITANIUM TETRACHLORIDE

BY GREGORY PAUL BAXTER AND GEORGE JOSEPH FERTIG

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The atomic weight of titanium in use at the present time, 48.1, depends entirely upon the concordant analyses by Thorpe¹ of titanium tetrachloride and tetrabromide. Both these substances are very sensitive to moisture, and must therefore be purified in an atmosphere free from water vapor. Thorpe recognized this difficulty, and in preparing material for analysis took precautions to avoid it. There is some question, nevertheless, whether these precautions were entirely adequate, and whether the products of earlier exposure to air were removed from the material analyzed. Furthermore, the analytical procedure did not include many necessary modern refinements. His result is, therefore, subject to considerable uncertainty.

Recent work in this Laboratory involving the purification of volatile halides by fractional distillation² led us to investigate titanium tetrachloride in the same way. Since the atomic weight of titanium found as the result of the analysis of the purified material is distinctly lower than the generally accepted one, and since the experimental work has been interrupted for an indefinite period, it seems worth while to present the preliminary result at this time.

¹ Thorpe, *Ber.*, **16**, 3014 (1883); *J. Chem. Soc.*, **47**, 108 (1885).

² See especially Baxter, Weatherill and Scripture, *Proc. Am. Acad. Arts Sci.*, **58**, 245 (1923).