tained in different apparatus under different conditions of the wall surface indicate that the contribution of the wall reaction to the total rate is small.

3. Both atoms and molecules can act as third bodies with an allowable greater efficiency for molecules.

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Azeotropic Hydrobromic Acid Solutions at Pressures of 100 Mm. to 1200 Mm.

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Some years ago we undertook as a part of the research program of this Laboratory a careful study of the boiling points, compositions, and densities of the azeotropic or "constant-boiling" acid solutions. The present paper represents the second acid thus far studied, the data on hydrochloric acid having been already published.[1]

Preparation of Hydrobromic Acid.—Two different methods were used in preparing the hydrobromic acid. The simpler was that of reduction of bromine by sulfur dioxide in the presence of sufficient water to give a solution of approximately constant boiling composition. This solution when freed of excess sulfur dioxide contained, of course, the equivalent amount of sulfuric acid, but the more volatile hydrobromic acid was readily removed from this by distillation. After this first distillation the HBr solution was treated with an excess of solid barium bromide and again distilled. The sulfate-free acid was then repeatedly redistilled, rejecting the first and the last portions, until a solution was obtained which was constant boiling at atmospheric pressure, and which also was free from any analytically significant impurity. In some cases we used bromine which we had carefully purified by the method of Baxter[2] while in other cases we used bromine of "reagent" quality, without further purification. The final acid solutions could not be distinguished.

The second method of preparation of hydrogen bromide solutions was that of direct synthesis from the elements. The hydrogen bromide solutions prepared by this method were indistinguishable from those prepared by the simpler method. Most of our acid was consequently made by the first method.

Preparation of Azeotropic Solutions.—The methods were much the same as those used previously for preparing constant boiling hydrochloric acid.[1] Due, however, to the particularly corrosive character of

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[1] Bonner and Branting, THIS JOURNAL, **48**, 2093 (1926); Bonner and Titus, *ibid.*, **52**, 633 (1930); Bonner and Wallace, *ibid.*, **52**, 1747 (1930).

[2] Baxter, *ibid.*, **28**, 1325 (1906).

hydrobromic acid it was found necessary so to prepare the samples that neither the vapor nor the liquid acid came in contact with any material but glass. The apparatus consisted of a 250-cc. Claissen flask with a thermometer sealed into one neck. The other neck was left open for filling. The distilling arm which was on the closed neck of the flask was sealed to a condenser tube of 6 mm. internal diameter. This was connected to the 250-cc. receiver as well as to the pressure control apparatus by means of ground glass joints. The distilling flask rested in a hole 3 cm. in diameter in a heavy asbestos plate, and the double neck of the flask was heavily insulated by wrappings of asbestos cord. The pressure control apparatus and the barometer have already been described.[1] The samples were prepared at the uniform distillation rate of approximately 3 cc. per minute. A bundle of fine capillary tubes served to prevent bumping. When first we began studying these solutions we frequently found them colored markedly red. On distillation this red color would accumulate in the residue, where it could be shown to be due to the presence of iron. This we eliminated by filtering through absorbent cotton all air or other gas which went into the pressure control apparatus. To exclude the possibility of air oxidation of hydrogen bromide we prepared all the azeotropic solutions in an atmosphere of carbon dioxide. We have also preserved our samples sealed under carbon dioxide. In preparing the apparatus for operation, about 200 cc. of hydrobromic acid solution, constant boiling at atmospheric pressure, was charged into the Claissen flask through the open neck. Connection was then made to the receiver and to the pressure control apparatus, and carbon dioxide (from a commercial cylinder) passed through the entire apparatus, until the air was well swept out. The open neck of the flask was then sealed off, and the desired pressure obtained, either by pumping out carbon dioxide, or by building up carbon dioxide pressure from the cylinder. This pressure having been established, the sample was boiled until about two-thirds of it had distilled over, the thermometer sealed in the neck of the flask indicating a steady boiling temperature. Distillation was then stopped, the receiver emptied, cleaned and dried, and the apparatus reassembled. After refilling the apparatus with carbon dioxide, and reëstablishing the pressure, distillation was begun anew and continued until about one-half the remainder had distilled over.

Analytical Methods.—The composition of the azeotropic solutions was determined gravimetrically, weighing the bromine as silver bromide. All usual precautions were taken, and all significant corrections applied. Densities were determined by use of a pycnometer, adjusted in a thermostat at 25 ± 0.05°. The volume of the pycnometer was 5.7865 cc.

Boiling points were determined by means of the platinum resistance thermometer and boiling point apparatus previously described in the work on hydrochloric acid.[1] About 10 g. of platinum tetrahedra were used to facilitate boiling without bumping.

Precision of Data.—The data presented on the composition of the constant boiling acids are in practically all cases means of the compositions of distillate and of residue. The maximum deviation from the mean is in general about 0.05% and in no case exceeds 0.1%. Correction to vacuum has not been made, as it falls outside this limit of precision. Calibrated weights were used, and any significant corrections applied. Densities as given are also the means of the densities of distillates and of residues. These have been corrected to vacuum, and for weight calibrations, and are reproducible to about 0.01%. The deviation between the densities of a distillate and of the corresponding residue was, however, generally greater than this, being at the most about 0.05%. This corresponds to a difference in composition between distillate and residue of at most 0.1%. It has already been pointed out[3] that density determinations constitute the most sensitive method of ascertaining whether a given distillate is really "constant boiling."

Pressures were measurable to 0.5 mm. or less and reproducible to 1 mm. or less. Barometric readings have been constantly compared with those of the local Weather Bureau. The boiling points as given are reproducible to about 0.02°. The data all are assembled in Table I.

TABLE I

Pressure in mm.	B. p. in °C.	Density at 25°	Comp. in HBr
100	74.12	1.5116	49.80
200	90.35	1.5030	49.28
300	99.91	1.4961	48.83
400	107.00	1.4908	48.47
500	112.94	1.4866	48.19
600	117.82	1.4832	47.95
700	122.00	1.4802	47.74
800	125.79	1.4775	47.56
900	129.13	1.4752	47.40
1000	132.12	1.4733	47.27
1100	134.80	1.4716	47.14
1200	137.34	1.4700	47.03

The data on constant boiling hydrobromic acid have been well summarized by Ewing and Shadduck.[4] So far as we are aware, the data of Van Valkenberg and Bischof[5] are the only ones which have appeared since. Unfortunately the data are not very consistent. Disregarding the older ones, those which have accumulated since 1923 are still not satisfactory, as the following exhibit shows.

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(3) Hulett and Bonner, THIS JOURNAL, **31**, 391 (1909); Foulk and Hollingsworth, *ibid.*, **45**, 1220 (1923).

(4) Ewing and Shadduck, *ibid.*, **47**, 1901 (1925).

(5) Van Valkenberg and Bischof, *J. Colorado-Wyoming Acad. Sci.*, **1**, 25 (1929).

Observer	Pressure	Boiling point, °C.	Composition, % HBr
Carrière and Cerveau[6]	760 mm.	126	47.5
Ewing and Shadduck	760 mm.	125	47.79
Bonner, Bonner and Gurney	760 mm.	124.3	47.63

These represent the most precise data available for a pressure of 760 mm. Those of Carrière and Cerveau cannot be regarded as of high precision as the composition was determined by titration. Ewing and Shadduck, on the other hand, made very careful gravimetric analyses, but apparently used no criterion to show that they were dealing with actually azeotropic solutions. The same criticism is to be made of Van Valkenberg and Bischof's data. Their work was done at pressures between 630 and 700 mm., but they neglected to check the composition of the residue to show that it was the same as that of the distillate. The four pressure-composition points reported by Van Valkenberg and Bischof do not fall on a smooth curve, and the best curve which can be drawn through them has a very much steeper slope than has our curve at any point. Their boiling points, however, fall very close to our boiling point curve.

We believe that our data are the most consistent yet presented on azeotropic hydrobromic acid solutions. They are not so precise as those available on hydrochloric acid solutions.

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(6) Carrière and Cerveau, *Compt. rend.*, **177**, 46 (1923).