[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF UTAH]

THE COMPOSITION OF HYDROCHLORIC ACID OF CONSTANT BOILING POINT

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In 1909 Hulett and Bonner[1] published a method for the preparation of standard hydrochloric acid solutions, based upon the constancy of composition, at a definite pressure, of the constant-boiling-point solutions of hydrogen chloride in water. This is a very convenient method, and its reliability has since been corroborated by Morey[2] and by Hendrixson.[3] More recently, Foulk and Hollingsworth[4] have taken exception to the values given by these previous experimenters, and have offered a more precise determination of the composition of the acid of constant boiling point. The correction offered amounts to about one part per thousand on the value given by Hulett and Bonner. Since all the work cited has been done at pressures near to sea level, it has seemed important to determine the composition of these solutions of constant boiling point in the vicinity of this Laboratory, where the average barometric pressure is 640 mm.

Experimental Part

In making the distillations for obtaining the solutions of constant boiling point, we have used the controlled-pressure method of Foulk and Hollingsworth.[4] The distilling flask was fitted with a Beckmann thermometer and was provided with a few grams of platinum tetrahedra to prevent overheating. The flask was electrically heated. In preparing the solutions of constant boiling point, concentrated acid of C.P. grade was diluted to a specific gravity of 1.1. Two distillations of one liter each were then made, and the first 500 cc. of each was discarded. The last 500 cc. of these two distillates were then combined and redistilled. Of this the first 700 cc. was discarded, the next 200 cc. was taken as the sample and 100 cc. was left in the flask. The residue was not analyzed. All distillations were made at the rate of 250 cc. per hour.

The Beckmann thermometer used in this work was graduated to 0.01°, and the temperatures were estimated to 0.001°. The boiling point of toluene on this thermometer at 650 mm. pressure was 2.070°. We have not been able, however, to calibrate the instrument precisely. The boiling point of toluene at 650 mm., as given by Kahlbaum, *Z. physik. Chem.*, **26,** 616 (1898) is 105.3°. We have, therefore, recorded the approximate boiling point of the acid to 0.1°, as well as the actual Beckmann-thermometer

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[1] Hulett and Bonner, THIS JOURNAL, **31,** 390 (1909).

[2] Morey, *ibid.*, **34,** 1027 (1912).

[3] Hendrixson, *ibid.*, **37,** 2352 (1915).

[4] Foulk and Hollingsworth, *ibid.*, **45,** 1220 (1923).

reading. By determining precisely the boiling point of toluene at 650 mm., the precise boiling points of the acid can be obtained. If this were once done, hydrochloric acid of constant boiling point would constitute a very convenient fixed point in thermometry. Foulk and Hollingsworth[4] have already shown the constancy of the boiling point, and the acid of constant boiling point is much more easily prepared than toluene is purified.

The compositions of the solutions of constant boiling point were determined gravimetrically, by precipitation of silver chloride. The weight of silver chloride obtained was always about 1.3 g., the volume of filtrate was about 200 cc., and of washings about 300 cc. Under these conditions the solubility of silver chloride is negligible. The filtrate and washings were filtered twice through 1cm. disks of ashless filter paper, and the asbestos fibers so recovered were added to the crucibles before the final weighing. The silver chloride was dried to constant weight at 260°, repeated trials having shown that precipitates so dried suffered no loss in weight on being fused. Redistilled water was used throughout, and the silver nitrate employed was carefully purified. All weights and volumetric apparatus were calibrated, and all weighings were reduced to vacuum. The densities were determined by weighing in a pycnometer of the Ostwald-Sprengel type, the temperature being 25° ± 0.02°. Table I gives the results of our work.

TABLE I

RESULTS

Pressure Mm. of Hg	Approx. b. p., °C.	Beckmann thermometer reading	Density	HCl, %	Air weight per mole, g.
620	103.3	0.073	1.0986	20.560	177.194
630	103.7	.472	1.0984	20.532	177.427
640	104.1	.875	1.0983	20.504	177.671
650	104.5	1.266	1.0982[a]	20.471[a]	177.967
660	104.9	1.642	1.0981	20.438	178.244
700	...	...	1.0975	20.351	179.008
760[b]	108.54	...	1.0974	20.242	180.170

[a] Interpolated.

[b] Data from Hulett and Bonner.

We have given special attention to the 640mm. distillate, as that is our average barometric pressure, and such distillations can be made with a minimum correction. The composition for this solution rests upon analyses made on three different samples whose density differed not more than one part in 10,000. The result given, 20.504% of hydrogen chloride, is the mean of 18 analyses, with a maximum deviation from the mean of 0.003% or about three parts in 20,000.

We have not attempted to interpolate between our values and the sea level values. The slope of the curve given by the data of Hulett and Bonner, or those of Foulk and Hollingsworth, is markedly different from the slope of our curve covering the same pressure difference, namely, 40 mm. It is apparent that the composition is not a linear function of the pressure under which distillation is accomplished. The same thing is apparent in the work of Roscoe and Dittmar[5] which is the only work covering a long pressure range. The importance of these solutions of constant boiling point is such that this work of Roscoe and Dittmar should be repeated with all possible precision. We hope to undertake this in this Laboratory during the coming year.

Summary

A precise determination of the compositions of hydrochloric acid of constant boiling point is given for pressures near 640 mm. It is pointed out that the composition of these acids is not a linear function of the pressure.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

ACTIVITY COEFFICIENTS OF SODIUM AND POTASSIUM BROMIDES AND IODIDES IN CONCENTRATED AQUEOUS SOLUTIONS

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The activity coefficients of some alkali metal halides have been obtained from measurements of electromotive forces of cells of the type, $Ag \mid AgX \mid MX(m) \mid M_xHg \mid MX(m_0) \mid AgX \mid Ag$, by a number of investigators. Thus, MacInnes and Parker[1] and MacInnes and Beattie[2] have determined the activity coefficients of potassium chloride and lithium chloride in concentrations ranging from 0.01 to 0.5 *M* and from 0.01 to 3 *M*, respectively. Allmand and Polack[3] have measured the activity coefficient of sodium chloride by a similar cell in dilute and concentrated solutions, and Pearce and Hart[4] have studied potassium bromide solutions. With the idea of making these data more complete, we have undertaken an investigation of the activity coefficients of concentrated aqueous solutions of potassium and sodium bromides and potassium and sodium iodides and for this purpose have measured the cells

$$Ag \mid AgBr \mid NaBr(m_2) \mid Na_xHg \mid NaBr(m_1) \mid AgBr \mid Ag$$
$$Ag \mid AgBr \mid KBr(m_2) \mid K_xHg \mid KBr(m_1) \mid AgBr \mid Ag$$
$$Ag \mid AgI \mid NaI(m_2) \mid Na_xHg \mid NaI(m_1) \mid AgI \mid Ag$$
$$Ag \mid AgI \mid KI(m_2) \mid K_xHg \mid KI(m_1) \mid AgI \mid Ag$$

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[5] Roscoe and Dittmar, *J. Chem. Soc.*, **12**, 128 (1860); *Ann.*, **112**, 343 (1859). Roscoe, *Ann.*, **116**, 213 (1860).

[1] MacInnes and Parker, THIS JOURNAL, **37**, 1445 (1915).

[2] MacInnes and Beattie, *ibid.*, **42**, 1117 (1920).

[3] Allmand and Polack, *J. Chem. Soc.*, **115**, 1020 (1919).

[4] Pearce and Hart, THIS JOURNAL, **43**, 2483 (1921).