

fluorine is favorable. With mole ratios of less than 1/1 some crystals which could not be isolated but which may have been an acid sodium fluocolumbate were observed.

The properties of sodium hexafluocolumbate and sodium heptafluocolumbate have been examined.

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## Preparation of Constant Boiling Hydrochloric Acid. Rate of Approach to Equilibrium

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In the first precise paper on constant boiling hydrochloric acid Hulett and Bonner<sup>1</sup> pointed out that starting with acid of density 1.09 to 1.15 and distilling 75% of the starting volume resulted in the remaining distillate being well within the constant boiling region. They also showed, however, that equilibrium was attained after only 60% of a solution of density 1.10 had been distilled. The attainment of constant distillate density served to indicate equilibrium.

In view of the importance of the preparation of constant boiling hydrochloric acid for use as a primary standard in analytical chemistry, it was considered desirable to extend the above study over a larger range of starting densities, and to follow the course of density change during complete distillations in each case. It has been found that not only are the statements given in the first paragraph confirmed but furthermore when starting with acid of density about 1.06 attainment of equilibrium is extremely slow, whereas with acid of density about 1.14 it is fairly rapid in spite of these two density values being about equidistant from the equilibrium value. The results are given in Figs. 1 and 2. The last fractions are again represented in the latter, along with the check values, all on a very large scale.

### Experimental

All hydrochloric acid was pre-distilled and its density precisely determined after appropriate dilution. In the regular runs 300 ml. was distilled using a 1-liter distilling flask with the side-arm fitting into a straight condenser, forming an acid seal. Sintered quartz kept the acid boiling smoothly and collection was made in nine fractions in 25-ml. Erlenmeyer flasks, leaving about 6 ml. of residue. There was a loss of about 10 ml. which was considered as distributed evenly and so was ignored. The first few ml. of each ninth of the approximately 294 ml. actually distilled (32.7 ml. should be a fraction) was used for rinsings and the 28 ml. used for density determinations was then separately collected. In Fig. 2 there are horizontal lines

for the typical ninth fraction and for the residue, as well as for the analyzed portion of the ninth fraction. Samples were collected without use of an adapter although this entailed a small but negligible amount of evaporation and density change.

Densities were determined at 24.97° (to less than 0.10°) in glass-stoppered volumetric flasks made especially for the work and used alternately for succeeding fractions. They each had a capacity of about 27 ml., calibrations in each case agreeing to less than 0.0010 ml. A proper counterpoise was employed for the glass, and the buoyancy effects on the contents and weights were corrected for, using the density 0.0010 gram per milliliter for air in Salt Lake City.

Separate samples of twice redistilled water were used in check work. Results from these were not plotted in Fig. 1 where the complete distillations are represented, but for the last five fractions dotted lines in Fig. 2 represent the checks. An average of run and check run values in Fig. 2 gives a density not over 0.00015 different from either, this value being considered as the precision here. Corrections were made here for the small barometric pressure differences between runs, all values being reduced to 647 mm. by means of the findings of Bonner and Titus,<sup>2</sup> who found in this range that 7 mm. pressure induced a density change of 0.0001 unit, increased pressure giving a lower density. Since the attempted precision in Fractions 6 and beyond for all curves except C and c, and for Fractions 8 and 9 of these last, was to several parts in the 5th decimal place, the values in Fig. 2 were plotted to that place. All other densities in both Fig. 1 and Fig. 2, as well as the unplotted check densities, were determined with an attempted precision of two parts in the fourth decimal place or better.

The first four fractions did not agree nearly so closely with their checks as the later fractions. The worst case was in Curve E, where Fraction I was 0.011 lower than its check although the starting density was 0.0005 higher. The other variations were smaller, being less than 0.002 after the first fraction except in Curve E and Curve e. All starting densities in the check runs were within 0.0010 density unit (gram per milliliter) of the values in the runs with which they were being compared. No check was made on Fraction 3 of Curve B but the fractions on each side checked satisfactorily. There was loss of gas in the first fraction in each of the higher curves, and this occurred into the second fraction for Curves E and e. This would cause a lowering of the plotted density from its true value in each case but would not affect the later densities of

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

(2) Bonner and Titus, *ibid.*, **52**, 633 (1930).

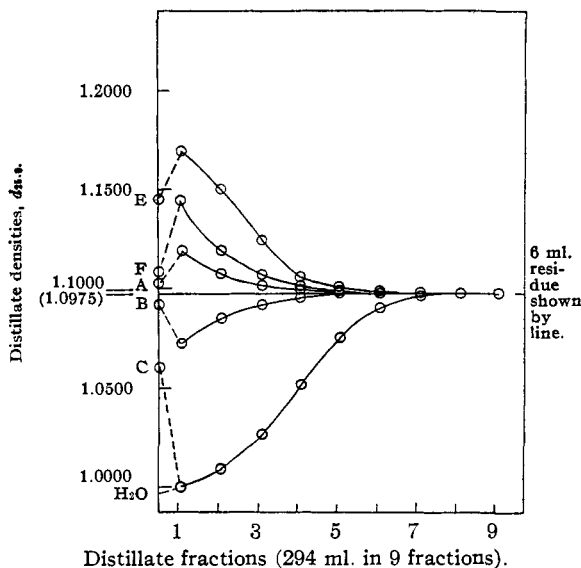


Fig. 1.—Densities of hydrochloric acid in nine distillation fractions.

course. Distillation rates were between 2.0 and 3.6 ml. per minute and barometric pressures between 643 and 649 mm.

It is considered that equilibrium in the distilling flask was attained as concerns outside barometric pressure in the light of recent unpublished results from this Laboratory by the senior author and Mr. William Tuddenham. With an apparatus such as used in the present paper the rate of distillation would have to be very much more rapid to cause even a 2 mm. (mercury) pressure excess in the flask.

### Results

The results embodied in Figs. 1 and 2 enable the conclusion to be drawn that it is safe to discard two-thirds of the distillate and then to keep most of the remaining one-third providing that the starting density is close to 1.10. The equilibrium density at 25.0° for acid distilled at 647 mm. pressure is slightly under 1.0975. Thus at 640 mm. it would be somewhat less than 1.0976, which is a little higher than the value 1.0973 obtained by Bonner and Titus.<sup>2</sup> The present work is not considered to be more precise than the latter how-

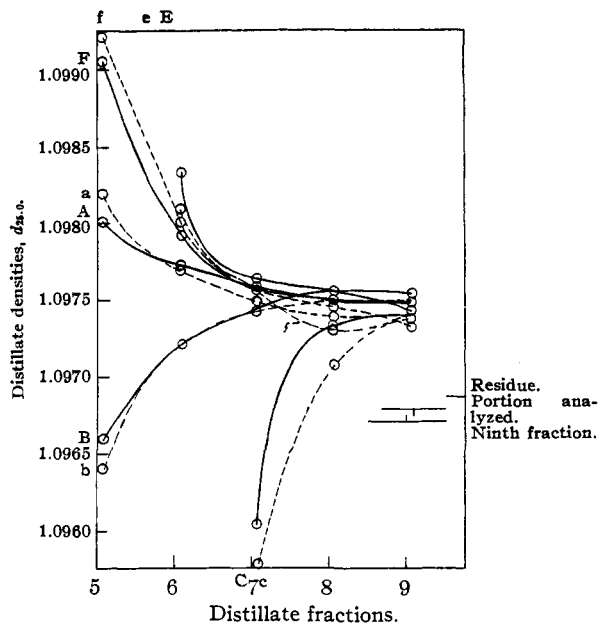


Fig. 2.—Densities of last fractions (large scale) (corrected to 647 mm. pressure).

ever, although the true value may be closer to 1.0976 than it is to 1.0973, since inspection of Fig. 2 would lead to this conclusion.

However, the chief contribution from this paper concerns the very slow approach to equilibrium when starting with acid in the low density range around 1.06, Curves C, c, as compared with Curves E, e which start at high densities even further removed from the equilibrium density.

The authors wish to express their thanks to W. D. Bonner of the University of Utah for his constructive interest in the work.

### Summary

Curves representing density of the distillate fractions have been presented for hydrochloric acid. Equilibrium is much more slowly attained starting with very weak acid than when starting with very strong acid.

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