centages too high. A more efficient baffle system would probably reduce or even eliminate the danger of contamination.[18] The entropy values of Keesom and Houthoff and the authors are shown in Fig. 6.

The authors wish to express their appreciation to Mr. G. St. J. Perrott, Superintendent of the Pittsburgh Experiment Station, U. S. Bureau of Mines, and to Dr. David F. Smith of the physical chemistry section for permitting the work of this investigation to be carried out at the Pittsburgh Station.

Summary

The specific heats of saturated liquid nitrogen and methane from the boiling point to the critical temperature have been measured.

The entropy and heat content of the saturated state have been calculated.

AMARILLO, TEXAS

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

THE COMPOSITION OF CONSTANT BOILING HYDROCHLORIC ACID AT PRESSURES OF 50 TO 1220 MILLIMETERS[1]

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RECEIVED OCTOBER 15, 1929 PUBLISHED FEBRUARY 6, 1930

Since Hulett and Bonner[2] published their paper on the preparation of standard hydrochloric acid solutions from constant boiling hydrochloric acid, their acidimetric standard has been checked by others, and its use has become fairly common.[3]

However, the only precise determinations of the compositions of these acids so far published are those made near sea level, and those made at the rather low barometric pressures near 640 mm.[4] The experiments of Roscoe and Dittmar, published 70 years ago,[5] remain the only work covering a considerable range of pressures. We have, therefore, determined the compositions and densities of various hydrochloric acids of constant boiling point between the pressures of 50 and 1220 mm. The procedure used was much that of Foulk and Hollingsworth[4] except that the pressure control apparatus was filled with mercury rather than with water. The compositions were determined gravimetrically, by means of silver chloride. The silver nitrate used was very carefully purified. The

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[18] This was suggested to the authors by Mr. E. S. Burnett.

[1] Arranged from the Master's Thesis of Albert C. Titus, University of Utah.

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

[3] See Morey, *ibid.*, **34**, 1027 (1912); Hendrixson, *ibid.*, **37**, 2352 (1915); Popoff, "Quantitative Analysis," P. Blakiston's Sons, Philadelphia, **1927**, 2d ed., p. 98.

[4] Foulk and Hollingsworth, THIS JOURNAL, **45**, 1220 (1923); Bonner and Branting, *ibid.*, **48**, 3093 (1926).

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

acid sample for each analysis was weighed, the samples being such that the weight of silver chloride was always about 2 g. The total volume of mother liquor and washings was always less than 1 liter, under which condition the correction to be made for dissolved silver chloride is negligible.[6] All weighings are reduced to vacuum and the weights used were carefully calibrated. The compositions given are each the mean of at least three concordant analyses, and the maximum deviation from the mean is never greater than 0.05%. They agree remarkably well with those given by Foulk and Hollingsworth[4] for 760-mm. pressure, and with those previously presented from this Laboratory for 640 mm.[4]

Densities were determined at 25 ± 0.02°, by means of an Ostwald–Sprengel type of pyknometer. The densities given are the means of never fewer than three independent experiments, and are precise to 0.01%. There is, however, a discrepancy of 0.1% between the density given here for the 640 mm. acid, and that given in the paper already referred to, for the same acid. We are unable to assign a cause for this, but we are convinced that the error lies in the previous data. Our density for the 760 mm. acid agrees within less than 1 part in 5000 with that given by Hulett and Bonner for the same acid. The barometer used was carefully compared with the U. S. Weather Bureau instrument in Salt Lake City. All necessary corrections have been applied, both to the barometer and to the pressure control apparatus. Pressures were maintained constant to within 1 mm. The following table gives the data assembled.

TABLE I

DENSITIES AND COMPOSITIONS

Pressure, mm.	Density	HCl, %
50	1.1118	23.42[a]
150	1.1073	22.520[b]
250	1.1042	21.883
350	1.1019	21.437
400	1.1010	21.235[b]
450	1.1002	21.075[b]
500	1.0993	20.916
540	1.0987	20.777[b]
600	1.0980	20.638[b]
640	1.0973	20.507
700	1.0966	20.360[b]
760	1.0959	20.222[b]
800	1.0955	20.155
1000	1.0933	19.734
1220	1.0915	19.358

[a] Result of a single analysis. [b] Interpolated.

When the percentage of hydrochloric acid in these acids is plotted as abscissas, using the corresponding densities as ordinates, the resulting graph is a straight line whose equation is

$$x = \frac{Y - 0.9966}{0.004912}$$

This equation is precise to about 0.05% within the range of ordinary barometric pressures. It is thus possible to prepare a sample of constant boiling hydrochloric acid at any convenient atmospheric pressure, deter-

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[6] See Richards and Wells, THIS JOURNAL, **27**, 486 (1905).

mine its density at 25°, and at once compute its hydrochloric acid content with a precision sufficient for any ordinary volumetric work. Any reference to the pressure of the distillation is thus avoided, it being only necessary to see that the barometric pressure is not changing rapidly during the preparation of the constant boiling acid.

Foulk and Hollingsworth, in the work already cited, found that the composition of the constant boiling acid was influenced markedly by the rate of the distillation. We have been unable to corroborate this. We have made, at various pressures, series of distillations in which the rate was varied from 1.7 cc. to 4.9 cc. per minute. These distillates were compared by determining the densities, and in no case did we find a difference in density as great as 1 part in 10,000. For example, in a set of ten such distillates, the mean density was 1.09709, with an average deviation of 0.00004 and a maximum deviation of 0.00009. We would conclude that the rate of distillation has a negligible effect on the composition. However, for the sake of convenience, we carried out all of our distillations at the uniform rate of 4.5 cc. per minute.

Résumé

We have determined the composition and density of constant boiling hydrochloric acid between pressures of 50 and 1220 mm.

We have given an equation by the aid of which the composition of any constant boiling hydrochloric acid may be computed from its density, at 25°. The use of this acid as a primary standard in acidimetry is thus simplified.

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NOTES

An Inorganic Stopcock Lubricant.—Up to the present time there has been no inorganic material discovered which compares favorably in all respects with stopcock grease, although there are many types of research in which such a material would be extremely valuable. The two main makeshift substitutes which have been used are moist phosphorus pentoxide and moist metaphosphoric acid, both of which leave much to be desired as lubricants for high vacuum work. The former tends to leak and to "freeze," while the latter "freezes" unless the stopcocks are turned very frequently.

During attempts to develop a more satisfactory lubricant for use in work at present in progress, the writer discovered that a thick, sirupy liquid with practically no tendency to crystallize on standing could be obtained by preparing a solution of the three phosphoric acids in one another. This mixture may be prepared with almost any desired viscosity by simply varying the proportions of the components. Due to