Summary.

It is shown in this paper that cadmium, copper, nickel, silver, and zinc (and probably other metals) can be precipitated from their solutions, completely and in weighable condition, by strong currents with the use of stationary electrodes, in substantially the same times as those required when rotating electrodes are employed.

The advantages of this are obvious: it means a return to the simplicity of apparatus and manipulation of the older and slower methods, while retaining the speed of the new. It should lead to the introduction of rapid methods of electro-analysis by those who have hesitated to employ them on account of the initial extra expense and the use of the machinery necessary for rotation.

CHEMICAL LABORATORY, SMITH COLLEGE.

A METHOD FOR PREPARING STANDARD HYDROCHLORIC ACID SOLUTIONS.

BY G. A. HULETT AND W. D. BONNER.

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We find that the "constant boiling" hydrochloric acid has a very definite percentage composition, is easily obtained and from it a standard solution of hydrochloric acid may be made directly and with ease and accuracy. In some of the older text-books on quantitative analysis it is recommended that a constant boiling hydrochloric acid be used to make approximate solutions and then standardized but we have found no notice of its being used as a basis for volumetric work.

It has long been known that hydrochloric acid, when distilled, will approach a point where it distils over unchanged in composition whether we start with a strong or weak acid in the still, and when this point is reached the residue in the still has the same composition as the distillate. We are concerned with the definiteness of the composition of the constant boiling acid and its variation with the pressure. The last point will be considered first, as the work of Roscoe and Dittmar[1] gave sufficient data on this point. These investigators determined the composition of the constant boiling hydrochloric acid obtained when distilling under pressures varying from 65 mm. to 2510 mm., and on plotting these results on a large scale it was found that a satisfactory curve could be drawn and it appeared that for the region with which we are concerned (660 to 860 mm.) that a change of 10 mm. in pressure produced a change of only 0.024 per cent. in the composition of the acid. For this region the acid obtained is about 20 per cent. hydrochloric acid and a change of 10 mm. in the barometric pressure caused a change of only one part in 4000, so it would seem that only for the most exact work need the baro-

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[1] *J. Chem. Soc.*, 1860, 128, and Roscoe, *Ann.*, 116, 343.

metric pressure be considered when preparing the constant boiling hydrochloric acid, but we have given below the exact values for the different pressures.

Information on the composition and reproducibility of the constant boiling acid was obtained by experiment. Samples of commercial "chemically pure" hydrochloric acid were diluted to various strengths and distilled from an ordinary distilling flask provided with a Liebig condenser. The distillate was rejected until the temperature was constant and then samples were taken at intervals and titrated as well as a sample of the residue. A number of experiments showed that it was necessary to distil over 3/5 of the acid taken before the constant boiling acid was obtained.

A 1/20° Beckmann thermometer was used and was carefully calibrated for the boiling point of water at 760 mm. This temperature of 100.00° was 10.12 on the scale and it was possible to read to 1/100° with this thermometer and the scale had been calibrated for this range of temperature. Starting with an acid of $d = 1.117$, the constant boiling reading was 18.40 with the barometer at 763.7 and this gave 108.53° as the observed temperature after all corrections had been made. A second experiment, starting with an acid $d = 1.131$ gave as the constant boiling point 108.55°. These experiments gave us an accurate determination of the constant boiling temperature of mixtures of hydrochloric acid and water—(108.54° at 763 mm.)—but showed that unless elaborate precautions were taken that this was not a reliable guide for the constant boiling acid. We have found, however, that when starting with an acid anywhere in the range of densities from 1.09 to 1.15 and distilling over 75 per cent. the remaining distillate and residue were well within the constant boiling region so the problem was, from the practical side, a very simple one.

In determining the composition of the distillates and residues it was found that titration with a standard alkali did not give the desired accuracy, the conductivity of hydrochloric acids of this strength changed only slightly with the composition, but it appeared from tables of densities of hydrogen chloride solutions, that in the vicinity of 20 per cent. a change of 0.00001 in the density made a change of only 0.002 per cent. in the composition and this accuracy was attainable with the Ostwald-Sprengel pycnometer used. A constant temperature bath was maintained at 25.00°, within 1/50°, and this was the temperature of all the determinations. A uniform method of drying and weighing the pycnometer was employed and all observations were corrected to vacuum weights so the densities (d_{25}) represent the ratio of mass to volume at 25°.

It was hardly expected that evaporation on an ordinary water bath would give a definite residue but two experiments were made:

500 cc. $d = 1.114$ evaporated to 152 cc. P 746 d_{25} of residue $= 1.10625$
500 cc. $d = 1.078$ evaporated to 137 cc. P 746 d_{25} of residue $= 1.10479$

The results are high and the agreement is not better than 0.3 per cent. This is probably due to the fact that air had access to the surface of the evaporating liquid producing the same effect as distilling under a diminished pressure—which was variable.

An experiment was made by boiling acids in ordinary beakers over a free flame:

500 cc. $d = 1.114$ boiled down to 162 cc. P 762.5 d_{25} of the residue 1.09816
500 cc. $d = 1.078$ boiled down to 137 cc. P 762.5 d_{25} of the residue 1.09775

Here the difference in composition of the residue is less, being only about 0.08 per cent., but they are both higher than the constant boiling acid by some 0.4 per cent. so it would seem that boiling in a beaker does not prevent the air from penetrating to the surface of the boiling liquid and producing the effect of boiling under diminished pressure (which increases the percentage of acid). We have not found an effect due to superheating, for the presence or absence of platinum tetrahedrons made no measurable difference in the composition of the constant boiling acid, but it was evident from the preceding experiments that it was quite essential to enclose the acid in a flask where the air was completely removed by the vapor and it was certain that acid was finally boiling in contact with its vapor alone and at the observed barometric pressure.

750 cc. of concentrated acid were distilled and 500 cc. of the distillate with density 1.158 were redistilled with the barometer at 758.5. The first 100 cc. of the distillate were rejected and the densities of the following portions were taken:

100–120	d_{25} = 1.1188
170–120	d_{25} = 1.1001
240–260	d_{25} = 1.0975
360–380	d_{25} = 1.09625
Residue	d_{25} = 1.09615

Here the portion 360–380 cc., counting from the beginning, and the residue differ by only 0.02 per cent. of hydrochloric acid. The exact composition will be given later.

1260 cc. of acid d = 1.103 were distilled at 760.0, after 900 cc. had been distilled over the following 210 cc. and the residue of 150 cc. were examined with the following results:

900–1110	distillate	d_{25} = 1.09615
Residue		d_{25} = 1.09625

900 cc. d = 1.106 were distilled at 755.6 mm. and 740 cc. of the distillate rejected; the following 140 cc. showed d_{25} = 1.09621, the residue was lost.

1000 cc. acid d = 1.089 were distilled at 762 mm. until 840 had distilled over—and the following 130 cc. showed d_{25} = 1.09612. The residue of 840–970, only 30 cc., was not examined. It must be borne in mind that the residue will contain all the nonvolatile impurities and chlorides the acid has collected so the density of the residue, or analysis as silver chloride, would be open to question, unless the acid had been redistilled, but the distillate is free from this source of error and we have found that ordinary commercial "muriatic acid" will give reliable results.

A determination of the composition of the constant boiling acids obtained was made by the silver chloride method. After making the density determinations the content of the pycnometer was washed into a liter flask and diluted to the mark. Samples of 50 cc. were taken for analysis and the silver determined as silver chloride with the aid of a Gooch crucible, taking the usual precautions. The flask and pipette were calibrated to hold a *volume* at 20° and the temperature was controlled, and thus the silver chloride weighed represented the chlorine in 1/20 of the weight of the acid in the pycnometer or for 3.5694 grams (air weight) of the constant boiling distillate and the results of these analyses are given in the last column of the following table;

	D_{25} of distillate.	P.	D_{25} cal. for 760 mm.	AgCl from 1.5694 g. of the distillate.
1.	1.09625	758.5	1.09624	....
2.	1.09615	760.0	1.09615	*a* 1.2491
				b 1.2480
3.	1.09612	7622.0	1.09615	*a* 1.2473
				b 1.2469
4.	1.09621	755.6	1.09625	*a* 1.24863
				b 1.24857

From these results we take the density of the constant boiling distillate at 760 mm. to be d_{25} = 1.09620 and 1.5694 g. air weight of this distillate equivalent to 1.2486 g. AgCl. Taking silver to be 107.88, chlorine 35.46 and hydrogen 1.008 we have for silver chloride 143.34 and for hydrochloric acid 36.47. On this basis a molecular weight of silver chloride would require 180.170 g. (air weight) of the constant boiling acid and this weight would contain one mol. (36.47 g.) of HCl or 20.240 per cent.

By starting with hydrochloric acid about d = 1.10, made up with an ordinary hydrometer or sp. gr. balance, and distilling off 3/4 of the liquid taken, the following distillate should not differ by more than one part in 10000 from the figures given in the following table. This constant boiling acid is not hydroscopic or noticeably volatile and may be easily weighed in a little flask. By using a capillary pipette joined to a piece of flexible rubber tubing, to adjust the last amount of acid, it is a very simple matter to weigh out 180.170 g. to less than 10 mg. and this will give a normal solution with an accuracy that is seldom attained even with very elaborate precautions.

164.42 cc. of this constant boiling acid (at 25°) contains a mol. of hydrochloric acid and one cubic centimeter contains 6.08 millimols of hydrochloric acid, figures which may be of use in making up solutions, but volume measurements are less accurate than weight determinations, while the latter are free from variations with the temperature. Only for the most accurate work need one consider the pressure under which the acid is distilled if the barometer is in the vicinity of 760, but we have calculated the following tables from the results obtained in this work and the values given by Roscoe and Dittmar.

Pressure.	Per cent. HCl.	Grams constant boiling distillate for 1 mol. HCl.
770	20.218	180.390
760	20.242	180.170
750	20.266	179.960
740	20.290	179.745
730	20.314	179.530

Both sulphuric and nitric acids give constant boiling mixtures but seem to be less desirable in several particulars than hydrochloric acid. which may serve as a reference basis, directly or indirectly, for most solutions.

We have found: That the temperature of the constant boiling hydrochloric acid is 108.54° at 763 mm. pressure;

That the density of the constant boiling distillate at 760 is d_{25} = 1.09620 and that it contains 20.242 per cent. of hydrochloric acid.

PRINCETON UNIVERSITY.