XVIII.—*On the Composition of the Aqueous Acids of constant Boiling Point.*

BY HENRY ENFIELD ROSCOE.

It is still a very generally received opinion, that a liquid which boils unchanged at a fixed temperature must be regarded as a chemically homogeneous body. This supposition is not, however, borne out either by theoretical considerations or by practical experience.

The proportions in which the constituents of a mixed liquid pass, on boiling, into the state of vapour depend upon the proportions in which the constituents are contained in the liquid, and upon the separate tensions of the vapours of these constituents at the temperature of ebullition. Although the laws which regulate the vaporization of mixed liquids are as yet far from being understood, it is easy to see that the relations between the several tensions and the proportions by weight of the two or more constituents may be such that, at a given temperature of ebullition, the composition of the vapour is identical with that of the liquid. As soon as this point is reached, the mixed liquid boils at a constant temperature without undergoing any change of composition, and in this respect does not differ from a uniform chemical combination. Such mixed liquids possess, however, other properties, by means of which they can be easily distinguished from definite chemical combinations. The characteristics by which a chemical compound is recognized, are generally considered to be (1), that the components of such a combination are united in quantities represented by some simple atomic relation; and (2), that this relation remains unaltered under a certain change of physical conditions.

From the experiments of Dalton, Mitscherlich, Millon, Bineau, and others, it has been hitherto supposed that most of the aqueous acids, and especially hydrochloric, hydrobromic, hydriodic, hydro-fluoric, nitric, and sulphuric acids, of very various degrees of strength, not only attain a fixed composition when boiled under the ordinary atmospheric pressure, but that the liquids thus prepared are definite chemical compounds of acid and water. In the present communication, my aim will be to show that this latter supposition is incorrect; that although liquids possessing constant

composition are obtained by boiling the above-mentioned acids under the ordinary atmospheric pressure, these bodies cannot be regarded as definite hydrates, but that the phenomenon of constant composition and fixed boiling-point is to be ascribed to the establishment of that particular relation between the weights and tensions of the constituents, by virtue of which acid and water are contained in the vapour in the same proportions in which they are present in the liquid. I shall show, in the first place, that the composition of the acids obtained by ebullition under the ordinary atmospheric pressure, does not, in the case of any of the acids examined, with one exception, agree with that of a simple hydrate; and, secondly, that in every case when these constant acids are brought under other physical conditions, such as when boiled under different pressures, or when a current of dry air is passed through them at different temperatures, they are decomposed and attain a different but constant composition, so that a mixture of acid and water may be made which, on vaporization at a given temperature, does not undergo any alteration in composition.

1. *Nitric Acid.*

Dalton was the first clearly to point out that mixtures of nitric acid and water, when boiled, undergo such a change that the weak mixtures lose water, and the strong mixtures lose acid, until the residual liquid attains a specific gravity of 1.42, and boils, under the ordinary atmospheric pressure, steadily at 120° C. This observation has since been confirmed by the experiments of Mitscherlich, Bineau, Millon, and Smith. The residual acid obtained by boiling either a weaker or a stronger acid was found by these chemists to possess an almost constant composition, the analyses giving an amount of nitric acid (HNO_6) varying from 66 to 70 per cent. on the liquid. From his own experiments Mitscherlich concluded, that this acid of constant boiling point contains 4 atoms of water to 1 atom of HNO_6 , whilst Bineau and others supposed that this acid consists of 3 atoms of water and 1 of nitric acid (HNO_6), corresponding to the well-known series of magnesian nitrates of the formula $\text{RNO}_6 + 3\text{HO}$.

Owing to the discrepancy in these statements, it appeared of interest to determine, as accurately as possible, in the first place, whether the acid obtained by distillation under the ordinary

atmospheric pressure has a constant composition; and, secondly, whether the relation between acid and water is one capable of expression in simple numbers. For this purpose, a quantity of strong acid was prepared by the usual processes,* and freed completely from lower oxides of nitrogen by passing a current of dry carbonic acid through the warm liquid. The acid thus prepared was perfectly colourless, and free from every trace of chlorine and sulphuric acid. The method of determination adopted, consisted either in volumetric analysis with a standard solution of caustic soda of exactly known strength, or in neutralizing the acid with a weighed quantity of pure fused carbonate of sodium, boiling the solution, and adding a small quantity of test acid or alkali to reach the exact point of neutrality, which was supposed to be attained when the litmus became blue. The quantity of acid employed for each determination was such, that the maximum analytical error, the amount of which was determined by control experiments, never attained 0·2 per cent. on the liquid. In order to check the two methods employed, an acid, which with test alkali was found to contain 68·00 per cent. of HNO_3 , and with pure carbonate of sodium gave 68·02 per cent. of HNO_3 , was neutralized with freshly precipitated carbonate of barium, the barium in solution being estimated as sulphate; 1·3368 grms. of the nitric acid yielded 1·6815 grms. of sulphate of barium, corresponding to 67·95 per cent. of HNO_3 .

The composition which aqueous nitric acid of various degrees of strength attains when boiled under the ordinary atmospheric pressure, was determined by diluting portions of the pure concentrated acid to a given extent with water, and, after analysis, distilling them in a small retort, the strength of the residual liquid being then accurately estimated. The experimental results are contained in the following Table, in which Column I gives the volume of acid employed; Column II, the percentage quantity of real acid (HNO_3) contained in the liquid before distillation; Column III, the volume of liquid remaining in the retort; and Column IV, the percentage quantity of real acid (HNO_3) contained in the residual liquid after distillation.

* Millon's statement respecting the difficulty of separating from the distillate the sulphuric acid used for concentrating the nitric acid was not confirmed. Strong nitric acid was easily obtained free from every trace of either sulphuric or hydrochloric acid.

TABLE 1.

No.	I.	II.	III.	IV.
(1)	25 cbc.	99·8	5 cbc.	95·8
(2)	25 "	95·2	5 "	84·8
(3)	25 "	84·7	5 "	71·8
(4)	120 "	77·8	20 "	69·1
(5)	180 "	74·7	8 "	68·1
(6)	120 "	70·5	20 "	68·6
(7)	90 "	70·5	15 "	68·6
(8)	120 "	65·1	30 "	68·0
(9)	120 "	65·1	20 "	68·3

From these experiments it is seen, that nitric acids of widely different degrees of concentration attain on boiling a composition varying from 68 to 69 per cent. of real acid. The slight differences in the composition of the residue here observed, arise from the impossibility of performing the experiments under the same physical conditions, as overheating the vapour, unequal exposure to air, &c., cannot be avoided. This is proved by comparing the results of a second series of experiments, detailed in Table 2. The distillation was, in these instances, effected in a small bulb-tube retort, blown before the lamp, in which the ebullition in presence of platinum proceeded more regularly and quietly than in the larger retort before employed; the liquid was also reduced by boiling to the same volume in every experiment, and thus the causes of variation as much as possible avoided. The designation of each column remains the same as in Table 1.

TABLE 2.

No.	I.	II.	III.	IV.
(1)	20 cbc.	70·2	5 cbc.	68·1
(2)	20 "	68·3	5 "	68·0
(3)	20 "	68·3	5 "	67·9
(4)	20 "	66·9	5 "	68·0
(5)	20 "	66·2	5 "	68·0
(6)	20 "	66·2	5 "	68·0
				Mean 68·00

Hence we may conclude:—

(1.) That the residual liquid obtained by boiling aqueous nitric acid of various degrees of concentration under the ordinary atmospheric pressure possesses a constant composition.

(2.) That the liquid thus obtained contains 68·0 per cent. of real acid, and that, therefore, the proportion between acid and water cannot be represented by any simple atomic relation, the formula $\text{HNO}_6 + 3\text{HO}$ requiring 70·0 per cent. of HNO_6 .*

The boiling-point of the acid, containing 68·0 per cent., was found to be $120^{\circ}\cdot 5$ C., under a barometric pressure of $0^{\text{m}}\cdot 735$; its specific gravity at $15^{\circ}\cdot 5$ C. was shown to be 1·414 as a mean of two determinations.

Distilled at other temperatures, the relation of real acid to water will, if the phenomenon of constant boiling-point depends altogether on physical causes, be found to be a different one. In the following experiments, aqueous nitric acid of various degrees of strength, was distilled under diminished atmospheric pressure, effected by placing the acid in a retort, the neck of which, drawn out and bent at an acute angle, passed through a solid caoutchouc stopper into a large bolt-head of 20 litres capacity, furnished with a divided manometer-tube, and communicating with the cylinder of a large air-pump. By this means the acid could be distilled under any wished-for pressure less than that of the atmosphere; by cooling the bolt-head, and by having a large absorbent surface of caustic soda in the interior of the flask, it was easy to keep the mercury in the manometer tube to within 5 millimetres of the required height during the whole course of the distillation. Table 3 contains the results of a series of such experiments; Column I, gives the pressure in millimetres of mercury, under which the distillation took place (*i. e.*, the barometric pressure,—the height of the mercurial column in the manometer-tube); Column II, the volumes of liquid employed; Column III, the percentage of real acid contained in this liquid; Column IV, the volume remaining after distillation; Column V, the percentage of real acid contained in the residual liquid.

* Calculated percentage composition of the hypothetical hydrates of nitric acid:—

	(1st)	(2nd)	(3rd)	(4th)
H. NO_6 . .	87 5	77 8	70 0	63 6
HO . .	12 5	22 2	30 0	36 4
	<hr/> 100 0	<hr/> 100 0	<hr/> 100 0	<hr/> 100 0

TABLE 3.

No.	I.	II.	III.	IV.	V.
(1)	75 mm.	150 cbc.	69.9	50 cbc.	66.7
(2)	50 "	20 "	68.3	5 "	67.2
(3)	75 "	150 "	66.9	50 "	66.7
(4)	68 "	20 "	66.5	5 "	66.8
(5)	75 "	20 "	66.2	5 "	66.5
(6)	75 "	120 "	65.1	30 "	66.7
(7)	150 "	150 "	66.9	50 "	67.6

Although showing a maximum difference of 1 per cent., owing to the acid being mechanically carried over by the irregular percussive ebullition, which it is impossible to prevent when nitric acid is heated under a diminished pressure, the results obtained are still sufficiently accurate to prove, that under a pressure of about 70 millimetres of mercury, when the boiling-point lies between 65° and 70° , a liquid possessing a constant mean composition of 66.7 per cent. of HNO_3 is obtained, whilst under a pressure of 150 millimetres, the equilibrium occurs when the percentage of acid reaches 67.6.

The distillation of nitric acid under pressures greater than that of the atmosphere, is accompanied by considerable experimental difficulties, owing to the impossibility of bringing the acid into contact with mercury. These difficulties were overcome by employ-

ing the following arrangement:—The bulb-retort (a) Fig. 1,

containing the acid, was connected by means of a solid caoutchouc stopper with a strong bottle (*b*), of one litre capacity, containing some dilute nitric acid; through the stopper passes a second tube, communicating with another similar bottle (*c*) containing mercury (*m*) and a strong solution of caustic soda (*s*); a divided manometer tube (*d*) dipped into the mercury, and a third tube (*e*) passing through the stopper of the bottle (*c*) could be placed to any required depth into a reservoir of mercury. The bottle (*b*) being immersed in cold water, the increase of pressure was attained by pushing the glass bucket (*g*), filled with pieces of marble, into the dilute acid, by means of the stiff iron wire (*f*), working perfectly air-tight through the caoutchouc stopper. As soon as the mercury in the manometer tube had attained the wished-for height, and the gas issued from the extremity of the tube (*e*) under the mercury, a portion of the acid in the retort was distilled over, and the residue afterwards analyzed. By withdrawing the marble from the acid and again immersing it when required, the pressure was kept tolerably constant during the whole course of the experiment. The numbers in the following Table show, that distilled under a mean pressure of 1,220 millimetres of mercury, beyond which it was found inconvenient to operate, the composition of the residual liquid reached 68·6 per cent. of real acid, being a deviation from the acid distilled under ordinary pressures of 0·6 per cent.

TABLE 4.

No.	I.	II.	III.	IV.	V.
(1)	1260 mn.	20 cbc.	70·5	5	68·8
(2)	1210 „	20 „	68·3	5	68·7
(3)	1190 „	20 „	68 0	5	68·4
Mean 1220.			Mean 68·6		

The numbers in the columns have the same signification as those in Table 3, except in the first, in which the sum of the heights of the barometric column and the column of mercury in the manometer tube is given.

As it has thus been shown that aqueous nitric acid is a liquid which does not give rise on distillation to bodies possessing a simple atomic constitution, but that for each temperature a liquid

having a constant composition is obtained, it appeared of interest to determine for lower temperatures the composition of the acid unalterable by vaporization.

For this purpose, air, completely dried over sulphuric acid and phosphoric anhydride, was passed through the nitric acid contained in the burette-shaped vessel, Fig. 2, until no further change in composition was observed. The requisite temperature was obtained by immersing the burette in a large water-bath, the heat of which was kept constant, a weighed U-tube, containing phosphoric anhydride, being placed between the burette and the drying apparatus, to ensure all absence of moisture. Experiments thus conducted for every temperature, show that a point is reached at which the composition of the aqueous acid undergoes no further change by vaporization. In Table 5, Column I gives the percentage of real acid in the liquid before the experiment; Column II, the percentage after the experiment; Column III, the fraction of the original volume of acid remaining after the experiment; Column IV, the duration of the experiment in hours.

Fig. 2.

TABLE 5.

Passage of dry air through acid at 100° C.

No.	I.	II.	III.	IV.
(1)	68.0	66.2	$\frac{1}{4}$	2 hrs.
(2)	64.9	66.1	$\frac{2}{3}$	1 „
(3)	64.9	66.3	$\frac{1}{4}$	3 „

Passage of dry air through acid at 60° C.

(1)	68.0	66.9	} $\frac{1}{2}$	6 hrs.
(2)	66.9	65.7		9 „
(3)	65.7	65.2		30 „
(4)	65.2	64.9		9 „
(5)	64.9	64.8		20 „
(6)	64.9	64.8	$\frac{3}{4}$	8 „
(7)	64.8	64.5	$\frac{1}{2}$	9 „
(8)	64.5	64.4	$\frac{1}{3}$	9 „
(9)	64.0	64.5	$\frac{1}{2}$	8 „
(10)	64.5	64.5	$\frac{1}{4}$	6 „

Passage of dry air through acid at mean temp. of 13° C.

No.	I.	II.	III.	IV.
(1)	68·0	66·2	} $\frac{1}{2}$	48 hrs.
(2)	66·2	65·2		24 „
(3)	65·2	64·0		24 „
(4)	64·0	64·0		48 „
(5)	64·0	64·0		24 „
(6)	63·0	63·3		48 „
(7)	63·9	63·9		72 „
(8)	63·9	64·0		48 „

It is thus seen—(1.) That weak or strong aqueous nitric acid through which dry air is passed at 100°, attains a constant composition of 66·2 per cent. of real acid. (2.) That when air is passed through the same acid at 60°, the composition becomes constant at 64·5 per cent.; and (3.) That at the ordinary atmospheric temperatures—in mean 13°—the equilibrium is reached when the liquid contains 64·0 per cent. of real acid.

The ease with which strong nitric acid is decomposed, even at temperatures below its boiling point, is well known. It seems to be impossible to prepare the real acid HNO_6 by employing the usual method of distillation, rectification over sulphuric acid, and volatilization of the oxides of nitrogen by means of a current of dry air or carbonic acid. None of the chemists who have worked upon this subject appear to have had the real acid, and I have also failed to obtain it, although every care to ensure absence of moisture was taken; one colourless acid contained 99·8 per cent. of real acid, another 99·47 per cent. The former, nearly anhydrous acid, not only suffered decomposition on boiling, as is seen by reference to Table 1, but underwent alteration when a current of air perfectly dried over a large quantity of phosphoric anhydride was passed through the liquid at 15°. In seven hours, after which time three-fourths of the acid had been volatilized, the percentage of real acid had sunk to 98·77. This shows that nitric acid (HNO_6) undergoes decomposition, not only when vaporized at the boiling point, but also at the ordinary atmospheric temperatures.

II.—Sulphuric Acid.

We owe to Marignac the interesting and important observation, that real sulphuric acid (HSO_4) cannot be obtained by the

distillation either of a weaker aqueous acid or of a stronger fuming acid. The real acid can only be prepared by crystallisation, and, on boiling, is decomposed into anhydride, which is seen in the receiver, and a weaker acid remaining in the retort. Marignac showed that this weaker residual acid boils at 338°C , without undergoing change; and he further proved that aqueous sulphuric acid of every degree of concentration, whether containing more or less water than the real acid (HSO_4), attains this constant composition on boiling. From four separate determinations, Marignac found that this residual liquid contained 98.70 per cent. of real acid.

The following determinations have confirmed in every particular Marignac's conclusions. The analyses were made by weighing out the requisite quantities of pure fused carbonate of sodium, the exact point of neutrality being estimated by addition of small volumes of standard alkali and acid of well-established strengths.

(1.) Pure strong sulphuric acid, containing 93.4 per cent. of real acid, was distilled in a retort, until two-thirds of the liquid had been volatilized. The liquid remaining in the retort contained 98.7 per cent. of real acid.

(2.) An acid containing 98.37 per cent. of HSO_4 was distilled in a small retort, until one-fifth of the original volume remained. The residue contained 98.32 per cent. of HSO_4 .

(3.) An acid containing 98.37 per cent. of HSO_4 was boiled down in a porcelain capsule to one-third of its original volume. The residual liquid contained 98.45 per cent. of real acid.

(4.) An acid containing 100.33 per cent. of HSO_4 , and fuming in contact with the air at ordinary temperatures, was boiled down to one-eighth of its original volume. The residual liquid contained 98.8 per cent. of real acid.

(5.) Another portion of the same fuming acid, which a second analysis showed to contain 100.34 per cent. HSO_4 , was boiled to one-fourth of its original volume. The residual liquid contained 98.40 per cent. of real acid.

It thus appears not only that aqueous sulphuric, like aqueous nitric acid, attains an unalterable composition not corresponding to any definite hydrate, on distillation under the ordinary atmospheric pressure; but we also notice, what is very remarkable, that both the real acids, HNO_6 and HSO_4 , bodies which possess in other respects the characteristics of well-defined chemical com-

pounds, are decomposed on boiling, yielding that aqueous acid which remains unchanged at the temperature of ebullition.

III.—*Hydrochloric Acid.*

Bineau found that aqueous hydrochloric acid boiled under the ordinary atmospheric pressure, attained a composition of 20·2 p.c. of HCl, corresponding exactly to the formula $\text{HCl} + 16\text{HO}$, and this liquid he conceived to be a definite hydrate. In a research upon the absorption of hydrochloric acid and ammonia in water, published in vol. XII, page 128, of the Journal of the Chemical Society, which I made in conjunction with Mr. Dittmar, this result of Bineau's was, to a certain extent, confirmed, inasmuch as the acid of constant composition obtained by ebullition under the ordinary atmospheric pressure was found to contain 20·24 per cent. of HCl; but it was at the same time shown, that distilled under other pressures, or vaporized at other temperatures, this acid was decomposed, other liquids of constant composition being then produced, and the conclusion was therefore drawn that this hydrate has no real existence. The following Table 6, extracted from the above-mentioned memoir, gives the relation between the pressure under which the acid is distilled, and the composition of the constant liquid. The Column P shows the pressure in metres of mercury, under which aqueous hydrochloric acid must be distilled to attain the constant composition given in the next column.

TABLE 6.

Pm.	Percentage of HCl.	Pm.	Percentage of HCl.	Pm.	Percentage of HCl.	Pm.	Percentage of HCl.
0·05	23·2	0·6	20·7	1·3	19·3	2·0	18·5
0·1	22·9	0·7	20·4	1·4	19·1	2·1	18·4
0·2	22·3	0·76	20·24	1·5	19·0	2·3	18·3
0·3	21·8	0·8	20·2	1·6	18·9	2·4	18·1
0·4	21·4	0·9	19·9	1·7	18·8	2·5	18·0
0·5	21·1	1·0	19·7	1·8	18·7		
		1·1	19·5	1·9	18·6		
		1·2	19·4				

Hence it is evident:—(1.) That there exists for each pressure a corresponding aqueous hydrochloric acid, which undergoes no change in composition when distilled under this pressure, and therefore has a constant boiling point. (2.) That the composition of these aqueous acids is different for each pressure, a gradual change in pressure being accompanied by a gradual alteration in the percentage of hydrochloric acid.

When aqueous hydrochloric acid is vaporized by passing a current of dry air through the liquid at a given temperature, a similar point is reached beyond which no decomposition occurs. Table 7 contains the interpolated values obtained from the experimental results given in the original paper. The first column gives the temperatures; the second column gives the percentage of HCl contained in the acid, unalterable at the corresponding temperature.

TABLE 7.

T°.	Percentage of HCl.	T°.	Percentage of HCl.	T°.	Percentage of HCl.	T°.	Percentage of HCl.
0°	25.0	30°	24.1	60°	23.0	90°	21.4
5°	24.9	35°	23.9	65°	22.8	95°	21.1
10°	24.7	40°	23.8	70°	22.6	100°	20.7
15°	24.6	45°	23.6	75°	22.3		
20°	24.4	50°	23.4	80°	22.0		
25°	24.3	55°	23.2	85°	21.7		

IV. *Hydrobromic Acid.*

Löwig first observed that water saturated at the ordinary atmospheric temperature with hydrobromic acid gas loses acid when boiled, and that water containing but little gas in solution loses water under similar circumstances. Bineau showed that the composition of the acid obtained by boiling was constant, and, his experiments proving that such acid contained from 46.1 to 47.4 per cent. of HBr, he concluded that on distillation the hydrate containing 10 atoms of water is formed. According to theory, this hydrate should contain 47.38 per cent. of HBr, when the equivalent of bromine is taken as 80. On exposing aqueous acid of the above strength in a closed vessel over dried potash, or on passing a current of dry air through the acid, Bineau found that the residual liquid contained from 48.7 to 51.7 per cent. of

hydrobromic acid ; this he assumes to be a hydrate containing 9 atoms of water, composed theoretically of equal weights of water and real acid (HBr.)

For the purpose of determining the exact relation of the composition of aqueous hydrobromic acid to the temperature of ebullition, the acid was prepared by shaking together pure bromine, water, and phosphorus, added in small pieces from time to time, until the liquid became colourless, the strong fuming solution being freed by distillation from phosphorus and phosphoric acid. The pure and colourless acid thus prepared was diluted to a given extent with water ; and as soon as the percentage of real acid (HBr), which the diluted liquid contained had been estimated by accurate volumetric analysis with silver, it was boiled in a bulb-tube retort, under the ordinary atmospheric pressure, until a certain portion of the acid had distilled over, when the composition of the residue was determined by exact analysis with silver.

In Table 8 are seen the results of eight such distillations with aqueous hydrobromic acids of various degrees of concentration : Column I gives the barometric pressure under which the acid boiled ; Column II, the volume in cubic centimetres of acid employed ; Column III, the percentage of HBr contained in the original liquid ; Column IV, the volume in cubic centimetres of acid remaining in the retort after the distillation ; and Column V, the percentage of HBr contained in the residual liquid, being the mean of two analyses, which generally differed only in the second decimal place.

TABLE 8.

No.	I.	II.	III.	IV.	V.
	m.				
(1)	0·752	25 ebc.	45·54	8 ebc.	47·38
(2)	0·752	50 "	45·58	8 "	47·39
(3)	0·753	50 "	47·30	25 "	47·78
(4)	0·762	25 "	47·65	12 "	47·86
(5)	0·753	20 "	47·78	5 "	47·61
(6)	0·752	12 "	47·87	6 "	47·73
(7)	0·752	50 "	49·00	8 "	47·71
(8)	0·762	25 "	49·51	10 "	47·84

If the distillations are conducted under the same conditions, the compositions of the residual acids are identical (see Nos. 4 and 8); if the physical conditions (barometric pressure, and volume of liquid employed) are different, the acid may vary in composition about 0.1 or 0.2 per cent., as is seen in one or two of the numbers. From the foregoing experiments we see that aqueous hydrobromic acid when boiled under the ordinary atmospheric pressure of 0.76 of mercury, attains a fixed composition of 47.8 per cent. of real acid, or contains 0.5 per cent. more acid than Bineau's hypothetical hydrate. Under these circumstances it was found to boil constantly at 126°C. That the point of constant composition which aqueous hydrobromic acid attains on vaporization, is not solely dependent upon chemical attractions, but is mainly influenced by physical circumstances, is still more distinctly seen on examining the change which the aqueous acid undergoes when a current of dry air is passed through the liquid at a constant temperature. Through a liquid containing 47.65 per cent. of real acid, dry air was passed at the temperature of 16° for 50 hours; after the lapse of this time, the strength of the acid reached 51.8 per cent., and after the air had passed for 30 hours longer, the liquid contained 51.65 per cent. of real acid as a mean of two analyses, and had, therefore, attained the point of constant composition. Hence it is clear that neither of the supposed hydrates of hydrobromic acid has a real existence. In order to determine the point of equilibrium for other temperatures, perfectly dry air was passed through the acid at 100° contained in the burette Fig. 2, and the alteration which the liquid underwent was determined. The following results were obtained :—

Dry air passed through aqueous acid at 100° C.

					P.C. real acid.
(1)	1 vol. acid containing	48.0 p. c.	when reduced to	$\frac{1}{8}$ vol. contained	49.59
(2)	" "	48.05 "	" "	$\frac{2}{8}$ " "	49.07
(3)	" "	49.10 "	" "	$\frac{1}{2}$ " "	49.35
(4)	" "	50.10 "	" "	$\frac{1}{3}$ " "	49.35

The aqueous acid was also distilled under a greatly increased pressure by help of the arrangement represented in Fig. 3. (a) Fig. 3 is a small bulb blown before the lamp, to which is fused the glass tube (b), communicating by a solid caoutchouc stopper with

Fig. 3. the divided manometer tube (c), containing mercury. After the tube (c) had been filled with mercury to the requisite height, the acid was placed in the bulb, and then the drawn-out end closed before the blow-pipe. The distillation was now commenced and continued until the acid had diminished to a given volume, when the pressure was read off from the difference of height of the columns of mercury in the two tubes. For the purpose of obtaining the boiling point of the acid under these circumstances, a thermometer was inserted into the bulb-tube, and the apparatus made air-tight by a joint of caoutchouc and lead-foil carefully wrapped with copper-wire. Under a total pressure of 1·952 metres of mercury, the acid boiled at 153° C; analysis of the residual acid gave the following results :—

- (1) Acid containing 48·0 per cent. left after distillation a residual liquid containing 46·30 per cent. of real acid (HBr).
- (2) Acid containing 46·07 per cent. left after distillation a liquid containing 46·36 per cent. of real acid.

v. *Hydriodic Acid.*

Bineau concluded that the liquid of constant boiling point obtained by distilling a diluted or a saturated aqueous solution of hydriodic acid was composed of 11 atoms of water to one of real acid (HI). The residual acid contained, according to his experiments, from 56·3 to 57·2 per cent. of hydriodic acid, whilst, according to calculation, the 11-atom hydrate requires 56·39 per cent. of real acid. Aqueous hydriodic acid was prepared by leading into distilled water the gas evolved by heating a mixture of 20 parts of pure iodine, 14 parts of iodide of potassium and 1½ parts of phosphorus mixed with a little water. The acid thus obtained of any requisite degree of concentration was perfectly colourless when preserved out of contact with air, and although the acid was always distilled in a current of hydrogen, it still became slightly

coloured, but was not decomposed to such an extent as to affect the results of the analysis. The composition of the acid before and after the distillation was determined by volumetric analysis with silver; the results of these determinations, as is seen by reference to the following numbers, are closely concordant; care, however, must always be taken to have excess of silver present at the commencement of the analysis, otherwise some iodine is liberated by the free nitric acid.

TABLE 9.

Distillation of aqueous hydriodic acid under the ordinary atmospheric pressure.

Volume of liquid employed in each experiment 25 cbc.

„ „ remaining after each distillation 13 cbc.

Percentage of real acid taken.				Percentage of real acid in the residue.	
(1)	56.50	..	..	..	57.03
(2)	56.70	..	..	..	{ 56.93 56.94 56.90
(3)	57.24	..	..	..	57.03
(4)	57.17	..	..	..	{ 57.16 57.03 57.12
(5)	58.76	..	..	..	{ 57.03 57.10

Hence it is seen that the acid of constant composition which is obtained when aqueous hydriodic acid is boiled under the ordinary atmospheric pressure, contains 57.00 per cent. of real acid, and cannot, therefore, be considered to be a definite hydrate of hydriodic acid. The boiling point of this acid was found to be 127° C. under a barometric pressure of 0.774 metre. In order to ascertain the point of equilibrium for other temperatures, aqueous hydriodic acid was vaporized in a current of dry hydrogen gas at the temperatures of 16° and 100°. Table 10 gives the results of such experiments.

TABLE 10.

Vaporization of aqueous hydriodic acid in a current of dry hydrogen at ordinary atmospheric temperature.

	Temp.		Duration of the experiment.		Percentage of real acid taken.		Percentage of real acid in residue.
(1)	15°	..	32 hours	..	57·0	..	59·44
(2)	15°	..	41 „	..	59·44	..	{60·36 60·33
(3)	17°	..	15 „	..	60·03	..	60·27
(4)	17°	..	15 „	..	60·27	..	{60·42 60·39
(5)	19°	..	10 „	..	60·21	..	60·68
(6)	19°	..	6 „	..	60·68	..	{60·49 60·42

Vaporization of aqueous hydriodic acid in a current of dry hydrogen at 100° until half the liquid was volatilized.

	Percentage of real acid taken.				Percentage of real acid in residue.
(1)	56·98	..	..	..	58·49
(2)	59·78	..	..	..	58·26
(3)	58·21	..	..	..	{58·24 58·20

VI. *Hydrofluoric Acid.*

Aqueous hydrofluoric acid, when boiled under the ordinary atmospheric pressure, attains, according to Bineau, a constant composition corresponding to the formula $\text{HFl} + 4\text{H}_2\text{O}$, and containing 35·9 per cent. of anhydrous acid.

In order to verify this assertion, pure aqueous hydrofluoric acid was prepared by leading the gas evolved from a strong acid heated in a platinum retort into water, also contained in a platinum vessel; the acid thus obtained being then boiled under the atmospheric pressure, and the quantity of acid contained in the residual liquid determined, by throwing the acid, weighed in

a platinum capsule, into a vessel containing an excess of standard soda solution. The quantity of free soda was estimated by adding a slight excess of test acid, and the point of neutrality was considered to be reached when the litmus again became coloured blue on adding soda solution drop by drop in the cold. The results of a series of experiments thus conducted are seen in Table 11, in which Column I gives the volume of acid before boiling; Column II the percentage of HFl contained in the liquid before boiling; Column III the volume of HFl after boiling; and Column IV the percentage of HFl contained in the liquid after boiling.

TABLE 11.

I.	II.	III.	IV.	I.	II.	III.	IV.
80 cbc.	1·2	6 cbc.	5·8	12 cbc.	36·9	6	$\begin{cases} 37·4 \\ 37·2 \end{cases}$
80 "	6·2	40 "	11·8				
35 "	11·8	6 "	29·0	24 "	38·1	12	$\begin{cases} 36·1 \\ 36·0 \end{cases}$
80 "	16·5	6 "	$\begin{cases} 35·4 \\ 34·9 \end{cases}$	12 "	38·1	6	$\begin{cases} 36·8 \\ 36·7 \end{cases}$
20 "	32·0	2 "	35·2	24 "	38·9	12	$\begin{cases} 38·1 \\ 38·2 \end{cases}$
60 "	35·4	30 "	$\begin{cases} 36·4 \\ 36·2 \end{cases}$				
				40 "	39·0	20	$\begin{cases} 35·1 \\ 36·2 \\ 36·1 \end{cases}$
80 "	$\begin{cases} 36·4 \\ 36·8 \end{cases}$	60 "	$\begin{cases} 37·0 \\ 37·1 \\ 37·1 \end{cases}$	80 "	41·6	40	$\begin{cases} 39·1 \\ 39·0 \end{cases}$
24 "	26·5	12 "	$\begin{cases} 37·6 \\ 37·5 \end{cases}$				

From these experiments it is evident that when aqueous hydrofluoric acid is boiled in platinum vessels under the ordinary atmospheric pressure, it attains a composition varying from 36 to 38 per cent. of HFl. The great differences observed arising from the impossibility of keeping the physical conditions constant, under which the ebullition takes place. We may take the mean 37·0 per cent. as representing pretty closely the composition of the acid unalterable by boiling in the air. If a true chemical compound between acid and water were thus produced, such large

164 ROSCOE, ON COMPOSITION OF AQUEOUS ACIDS, ETC.

variations in the composition of the residual acid could not have been found. Vaporized at other temperatures, this constant hydrofluoric acid, containing 37·0 per cent. of HFl undergoes change. A portion of acid of the above strength, obtained by ebullition was placed in a platinum crucible over quick lime inside a leaden exsiccator closed with a lid having a sulphuric acid joint. After standing at a temperature of 15° C. for 4 days, the acid was found to contain, in two analyses, 36·4 and 36·6 per cent. of HFl; after remaining 4 days longer at the same temperature, the liquid contained 33·5 per cent. of acid; and when the acid had been standing for 2 more days at the same temperature over quick lime, it was found to contain 32·5 and 32·7 per cent. of acid. A weaker acid was next vaporized under like conditions; an acid containing 31·6 per cent. of HFl placed over quick lime at 15° attained, after 2 days, a composition of 32·1 per cent., and after a further exposure in the exsiccator for 4 days, two analyses showed that it contained 32·4 and 32·3 per cent. of HFl.

I beg to thank my assistant Mr. Schorlemmer for the able help which he has given me in carrying out the foregoing experiments.