

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE SEPARATION OF THE ELEMENT CHLORINE INTO ISOTOPES (ISOTOPIC ELEMENTS).

### The Heavy Fraction from the Diffusion.

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#### Introduction.

This paper will describe the experimental work begun in the year 1915 in this laboratory for the purpose of demonstrating the correctness of the hypothesis advanced by Harkins and Wilson. This was that chlorine, magnesium, and silicon, as well as neon, are mixtures of isotopes.<sup>1</sup> That neon contains an isotope of atomic weight 22, had already been discovered by Thomson<sup>2</sup> by the use of the positive-ray method, but at the time when this investigation was begun it did not seem that its presence in neon had been demonstrated by sufficient experimental evidence to make its existence altogether a certainty.<sup>3</sup> It appeared important, therefore, to demonstrate the existence of isotopic forms of at least one of the *light* elements by making an actual separation of one of the above mentioned elements into at least two fractions which would differ in their atomic weights, as determined by some chemical method. The prediction of the existence of the isotopes of the specific light elements mentioned above, was made on the basis of their chemical or mean atomic weights, and at that time the atomic weight of silicon was not known with a high degree of precision, while the atomic weights of magnesium and of chlorine, especially the latter, were considered to be very exact. For this reason and also because the deviation of the atomic weight of chlorine from a whole number is the largest known for any light element, it was decided<sup>4</sup> to attempt the separation of chlorine into its isotopes.

Of the methods suitable for the separation of substances of almost identical chemical properties such as isotopes either diffusion or the use

<sup>1</sup> Harkins and Wilson, *THIS JOURNAL*, **37**, 1371, 1390 (1915).

<sup>2</sup> Thomson, "Positive Rays of Electricity," Longmans, Green and Co., London, 1913, pp. 114-5.

<sup>3</sup> A letter of the date May 5, 1915, from the Cambridge laboratory written by Dr. F. W. Aston, states "For my own part I am fairly confident of the existence of neon and meta-neon, but I do not consider the results so far warrant a definite statement to the public. It is a pity that several authors of text-books seem to have jumped to the conclusion that such has been made." In December 1919 Aston secured good evidence from the positive-ray method that Thomson's discovery was correct, and that meta-neon of atomic weight 22 exists.

<sup>4</sup> Harkins and Hall, *THIS JOURNAL*, **38**, 53 (1916). The work was begun, however, by Harkins and Turner.

of a centrifugal machine seemed to give promise of the quickest attainment of results. Attempts were made to obtain funds for the construction of a centrifugal machine, since it seemed that a properly designed centrifuge might effect a comparatively rapid separation, but, since these attempts were unsuccessful, work was begun on a diffusion through the stems of church-warden pipes, as has been described by Harkins and Turner. A notice of the beginning of the experimental work was published in the year 1916.<sup>5</sup>

Not only was an apparatus constructed for the separation of chlorine, but Turner also built an apparatus containing about 12.2 meters of porous pipe stems, which was used in diffusing large quantities of hydrogen chloride. The diffusions were interrupted by the war, though a considerable amount of the latter gas was diffused by T. H. Liggett during the year 1917-8. In the autumn of 1919 the work was taken up by C. E. Broeker, who diffused fractionally both the light and heavy fractions. Preliminary analyses on the heavy fraction indicated that its atomic weight had been increased to 35.51, or by 0.05 unit, in February 1920, and a preliminary notice of the separation was published in the February, 1920, number of the *Physical Review*,<sup>6</sup> in *Science*,<sup>7</sup> and in *Nature*.<sup>8</sup> This seems to be the first separation of an element into isotopes, for which there is any satisfactory evidence, but attention should be called to the fact that Aston in 1913 made a preliminary report to the British Association on an attempt to separate neon into isotopes. Since he has not published the details of this work at any time, it is impossible to know what was accomplished, but Aston himself states that the results were not at all conclusive.<sup>9</sup> When the difficulties in purifying and handling neon,

<sup>5</sup> THIS JOURNAL, 38, 53 (1916).

<sup>6</sup> *Phys. Rev.*, 15, 74 (Feb. 1920).

<sup>7</sup> *Science*, N. S., 51, 289-91 (1920).

<sup>8</sup> *Nature*, 105, 230-1 (1920). A later note in *Nature*, Sept. 30, 1920, states that Brönsted and von Hevesy have succeeded in obtaining a difference of 1 part in twenty thousand in the density of mercury. This is less than one-thirtieth of the separation obtained earlier by Harkins and Broeker in the case of chlorine. A later paper in THIS JOURNAL, will show that Mulliken and Harkins have secured a separation of the isotopes of mercury more than twice as large as that reported by Brönsted.

<sup>9</sup> Aston, *Phil. Mag.*, 39, 450-51 (1920), states that in his early experiments he obtained a density difference of about 0.7, which would amount to 0.14 unit difference in atomic weight, provided no impurities were present. He states that his results were positive but not conclusive, and that in his later more elaborate apparatus he secured a density difference of only about 3/7 of the above amount, presumably because he used too great pressures in his apparatus. Aston's original report, *Report Brit. Assoc. Adv. Science*, 1913, p. 403, gave no details concerning this work. The higher value reported by Aston is altogether unreasonably large, if the theory of diffusion is taken into account, if the amount of neon produced was sufficient to be subjected to purification, since it would represent a cut of 470 thousand with a 100% efficiency. Thus even 10 liters of neon would give only 0.02 cc. While this amount might be increased by using

and the difficulty of detecting impurities, are compared with the relatively easy purification of hydrogen chloride, it will be seen that a difference of 0.05 in the atomic weight of chlorine is more conclusive than several tenths of a unit for neon, particularly when the neon is obtained, as in Aston's experiments, in very minute quantities.

In a recent note in *Nature* Aston<sup>10</sup> gives the impression that the separation of chlorine by ordinary diffusion methods is almost impossible, and considers that if we have obtained any separation it is very remarkable, since in the case of neon, where the separation is extremely difficult, only the 21st root is involved, while with chlorine it is necessary to "grapple with the 36th root." It should be pointed out that in considering only the roots involved Aston has come to a conclusion which is partly erroneous, since actually (see Table I) a smaller cut is required to produce an increase of 0.05 in the atomic weight of chlorine than to produce the same increase in the atomic weight of neon. Here the cut (C) is defined as the amount of the gas which passes into the diffusion tubes, divided by the amount of heavy fraction which is obtained after the diffusion. Thus, even apart from the great difficulty of securing a considerable quantity of pure neon, and the difficulties involved in keeping it pure, the theory indicates an additional disadvantage of neon for separations of this magnitude. However, as the deviation of the atomic weight increases the theory becomes more favorable to the neon, though the rarity of this gas and the other disadvantages mentioned above, together with the much smaller degree of precision in the determination of its atomic weight, more than counterbalance the advantages which arise.

The following table gives the values of the cut necessary to increase the atomic weight of chlorine and of neon by definite amounts, as calculated from the theory of Rayleigh, which relates to an ideal diffusion at low pressures into a vacuum.

TABLE I.

VALUES OF THE CUT  $(X + Y)/(x + y)$  NECESSARY FOR THE INCREASE OF THE ATOMIC WEIGHTS OF CHLORINE AND OF NEON BY DEFINITE AMOUNTS. A DIFFUSION OF THE HEAVY FRACTION. (Chlorine diffused as hydrogen chloride.)

(Percentage of isotope of atomic weight 37 in chlorine = 23, of atomic weight 22 in neon = 10.)

Increase of atomic weight.	Chlorine.		Neon.	
	Cut.	Corresponding enrichment.	Cut.	Corresponding enrichment.
0.05	160	1.1459	217	1.286
0.10	18,600	1.302	19,600	1.588
0.15	1,690,000	1.469	991,000	1.909
0.20	117,000,000	1.648	33,000,000	2.25

fractional diffusions it would seem practically impossible to secure the atomic weight change claimed upon enough material to allow of its proper purification with the amounts of neon at that time available.

<sup>10</sup> Aston, *Nature*, 105, 131 (1920).

Here  $x$  and  $y$  represent the number of mols of the light and heavy isotopes respectively in the heavy fraction after the diffusion, while  $X$  and  $Y$  represent the initial mol numbers. This table points out the important fact that it is easy to obtain an increase of 0.05 in the atomic weight of a *small quantity* of chlorine or of neon, and that it is also easy to obtain *very small quantities* of either with an increase of 0.10, provided the process is nearly 100% efficient in terms of the Rayleigh theory. However, if only very small quantities of the material are obtained, it is very difficult to make the thorough purifications which are necessary to give evidence that a separation has been effected. The table also shows that to attain an increase of 0.20 unit in the atomic weight, is very difficult, since to secure this by diffusing the heavy fraction in one operation would require that 130 tons of hydrogen chloride gas or 36 tons of neon be used provided one gram of product is to be obtained. While these amounts may be reduced considerably by the use of a system of fractional diffusions, this procedure, when used on gases, becomes very expensive either in terms of the original complications in the apparatus, or in the amount of labor necessary to keep a single system in operation.

In the above table the necessary enrichment ratio ( $r$ ) corresponding to the required change of atomic weight is equal to the value of  $(y/x)/(Y/X)$ . The equation of Rayleigh is

$$\frac{1}{C} = \frac{x+y}{X+Y} = \frac{X}{X+Y} r^{\frac{\mu}{\nu-\mu}} + \frac{Y}{X+Y} r^{\frac{\nu}{\nu-\mu}} \quad (1)$$

where  $\mu$  and  $\nu$  represent the diffusion coefficients of the light and heavy constituents respectively. This is easily converted into the form

$$\frac{C}{C_0} = \frac{1}{C} = r^{\frac{\mu}{\nu-\mu}} \left[ 1 + \frac{Y}{X+Y} (r-1) \right] \quad (2)$$

If it is assumed that the rates of diffusion of the gases vary inversely as the square roots of their molecular weights, this reduces to the following simple form.

$$\frac{1}{C} = r^{\frac{\sqrt{M_h}}{\sqrt{M_l} - \sqrt{M_h}}} \left[ 1 + h_0 (r-1) \right] \quad (3)$$

in which  $h_0$  represents the fraction of the heavy isotope  $Y/(X+Y)$  in the initial mixture, and  $M_l$  and  $M_h$  are the molecular weights of the light and heavy components of the mixture.

#### Relation between the Atomic Weights and Percentages of Two Isotopes and the Atomic Weight of the Mixture.

In order to calculate the cut necessary to produce a certain change in the atomic weight of a mixture of two isotopes, it is necessary to know

the fraction of each in the mixture, and this may be calculated from the mean atomic weight and the atomic weights of the pure isotopes. Let  $h_o$  and  $l_o$  represent the initial fractions of the heavy and light isotopes,  $h$  and  $l$  the similar values necessary to produce the required enrichment ( $r$ ), and  $M$ ,  $M_h$ , and  $M_l$ , the molecular weights of the mixture, of the heavy, and of the light fractions.

Then

$$l \cdot M_l + (1-l) M_h = M.$$

or

$$l = (M_h - M) / (M_h - M_l). \quad (4)$$

Similarly

$$(1-h) M_l + h M_h = M.$$

or

$$h = (M - M_l) / (M_h - M_l). \quad (5)$$

Divide (4) by (5):

$$r = \frac{h/l}{h_o/l_o} = \frac{M - M_l}{M_h - M} \cdot \frac{M_h - M_o}{M_o - M_l}. \quad (6)$$

By the use of Equations 3 and 6 the calculation of the cut necessary to produce any possible desired increase in atomic weight is very simple. It is obvious that the two equations may be combined into one.

$$\frac{Q_o}{Q} = \frac{1}{C} = \left[ \frac{M - M_l}{M_h - M} \cdot \frac{M_h - M_o}{M_o - M_l} \right] \frac{\sqrt{M_h}}{\sqrt{M_l} - \sqrt{M_h}} \left[ 1 + h_o \left( \frac{M - M_l}{M_h - M} \cdot \frac{M_h - M_o}{M_o - M} - 1 \right) \right]. \quad (7)$$

If we let  $k$  represent  $\frac{\sqrt{M_h}}{\sqrt{M_l} - \sqrt{M_h}}$  the "diffusion exponent," then the diffusion equation reduces to the simple form:

$$\frac{1}{C} = [1 + h_o (r-1)] \times r^k. \quad (8)$$

The value of the diffusion exponent ( $k$ ) as thus defined is  $-37.503$  for the isotopic forms of hydrogen chloride provided the only isotopes have molecular weights 36.008 and 38.008, while for neon it has the value  $-21.488$ , provided the only isotopes have atomic weights 20 and 22. It may be noted that the values of the diffusion exponents are not very different from the mean molecular weights, but that this is not a general relation unless the isotopes differ in atomic weight by 2, is shown by the fact that the exponent for lithium, with atomic weight 6 and 7, is  $-13.48$ . The exponent for the isotopic forms of hydrogen bromide of molecular weights 80 and 82 (bromine of atomic weights 79 and 81) is  $-81.492$ . A convenient rule for keeping in mind the magnitude of the exponent is that it has a value equal to half a unit more than the mean of the molecular weights of the isotopes when the two molecular weights differ by 2. Thus for isotopes of atomic weights 223 and 225, the exponent is  $-224.5$ . Obviously the exponent has larger values when the difference between the iso-

topes is only 1, and smaller values when it is greater than 2. When the difference is 1 the exponent is equal to half a unit more than *twice* the mean of the atomic weights, and when it is 4, it is equal to half a unit more than *one-half* the mean.

Equation 8 may be put in the form

$$\frac{1}{C} = \left[ 1 + l_0 (r-1) \right] \times r^{k+1} \quad (9)$$

or

$$\frac{1}{C} = r \frac{\sqrt{\sqrt{M_l}}}{\sqrt{M_l - M_h}} \left[ 1 + l_0 (r-1) \right] = r^{k'} \left[ 1 + l_0 (r-1) \right]. \quad (10)$$

The numerical value of  $k'$  is always one unit less than that for  $k$ , and the mean of these two values is for two isotopes equal to the mean of the molecular weights when the molecular weight difference is 2, twice the mean of the molecular weights when this difference is 1, and one-half the mean of the molecular weights when this difference is 4, or

$$\frac{k + k'}{2} = \frac{M_l + M_h}{M_l - M_h} \quad (11)$$

and

$$k + k' = 1. \quad (12)$$

This relation becomes less exact as  $M_l + M_h$  becomes smaller, and as  $M_l - M_h$  becomes larger numerically. That it is sufficiently exact for accurate calculations is shown by the fact that the value of  $k$  calculated above (by the use of 7-place logarithms) in the case of hydrogen chloride is  $-37.503$ , while the value given by Equations 11 and 12, is  $-37.504$ .

In superficial discussions of the separation of isotopes there has been a tendency to concentrate the whole attention upon the diffusion exponent, and the effect of the initial percentages of the isotopes in the mixture has been neglected. That these percentages have a very marked effect upon the enrichment ( $r$ ) necessary to produce a certain change of atomic weight, is obvious. For example an infinite value of the enrichment ratio will serve to increase the atomic weight of lithium only from 6.94, the mean value, to 7.00, that for the heavier isotope so, for larger atomic weight differences for this element, the diffusions must be carried out upon the light fraction. In spite of the fact that the heavier isotope of this element has an atomic weight higher by 16.67% than that of the lighter isotope, a very high percentage difference, the theory does not indicate that the conditions for the separation are very favorable, since the enrichment ratio has a very large value. It is obvious that when a mixture of isotopes is divided into two equal parts by diffusion, the decrease of the mean atomic weight for the light fraction is equal to the increase for the heavy fraction. The equations for the light fraction are being worked out in this labora-

tory, and will not be discussed further here as they will be presented in a later paper to be published in THIS JOURNAL by Mulliken and Harkins. The relations have been tested by an experimental partial separation of mercury into two fractions, one of lower and one of a higher density than ordinary mercury. The most favorable proportion for the separation of a mixture of two isotopes is 50% of each. Thus, it has been found that a cut of 18,600 is necessary to increase the atomic weight of chlorine from 35.46 to 35.56, an increase of 0.1, in case hydrogen chloride is diffused. The percentage of heavy isotope in this ordinary chlorine is 23. Now it is quite remarkable that if the initial mixture contained 50% of each isotope, the same increase in atomic weight would be brought about with a cut less than  $\frac{1}{10}$  as great, or of 1,670.

Since the percentage of the heavy isotope in the heavy fraction of both chlorine and neon approaches more closely to 50% as the diffusion proceeds, the separation becomes more and more easy when considered in terms of the cut (though much more difficult in the sense that the amount of material available decreases rapidly.) Thus while the first  $\frac{1}{10}$  of a unit increase in the atomic weight of chlorine requires a cut of 18,600, the second requires only one of 6,300, while the corresponding values for neon are 19,600 and 1,710, so the second increase of 0.1 unit in the atomic weight of neon requires only  $\frac{1}{10}$  the cut. However, from the practical standpoint the great number of fractional diffusions necessary to keep the quantity of material large enough to proceed with the operations, makes each successive  $\frac{1}{10}$  unit increase very much more difficult to attain.

#### **Apparatus for the Diffusion of Gases at Atmospheric Pressure.**

Of the methods for the diffusion of a gas through a porous wall, there is little doubt that the most efficient is what is termed a vacuum diffusion, in which the gas diffuses through the wall into as high a vacuum as can be maintained. The pressure on the high pressure or "heavy fraction" side of the wall is kept at a magnitude which is dependent upon the diameter of the pores in the wall, and at such a value (for example 10 mm. of mercury) that the mean free path of the gas is as great as the diameter of the pores, which should be a uniform diameter. The low pressure of the gas insures not only a molecular passage of the gas through the pores, but it also aids greatly in securing a good mixing of the gas.

There are, however, several objections to the diffusion at low pressures: (1) it is difficult to make the process automatic; (2) the volume of the gas per unit mass is greatly increased; and (3) it necessitates a more cumbersome method of collecting the heavy and light fractions. For these reasons it was decided, since a fair efficiency had been obtained in a separation of known gases, and particularly since a very good (about 60%) efficiency had been obtained in the separation of the isotopes of chlorine by Mr. Broeker

by diffusing at atmospheric pressure, to delay the use of the vacuum method until after the difference in atomic weight of the chlorine separated by this method had been definitely established by the use of this partly automatic apparatus.

The general procedure adopted is to generate hydrogen chloride at atmospheric pressure by dropping conc. sulfuric acid into conc. hydrochloric acid from a height of about 90 cm.,—in order to secure good mixing of the acids. After the first diffusion the sulfuric acid was dropped upon sodium chloride. The dried gas is passed through porous porcelain tubes, and the lighter fraction which consists of the diffusate which passes through the walls is swept away by a rapid current of purified air. The heavy fraction is that which passes through the system of tubes and remains inside. Both fractions are absorbed by condensation in the *surface* of a considerable amount of water. The apparatus though quite similar to that used in this laboratory by Dr. Turner and by Mr. Broeker, but not described by them, is greatly improved in many particulars. It was designed to care for 1000 liters of hydrogen chloride per day, at atmospheric pressure.

Only acids of high purity were used in the work, and the hydrogen chloride produced came in contact with only pure sulfuric acid, glass, porous porcelain, and a very small area of paraffin, from the time it left the generators until it was absorbed in distilled water of the "conductivity" grade.

Since according to the Rayleigh theory the enrichment of the heavy fraction with respect to the heavy constituent depends only upon the fraction of the original gas that remains inside the diffusion tubes, and since this fraction changes very rapidly with the rate at which the gas is fed into them from the generator, a flow meter was placed in the line leading from the generator, and the evolution of gas was so regulated that the flowmeter gave a constant reading.

Flowmeters were also placed in all of the air sweep-out lines for each diffusion tube jacket, since it was necessary to reduce the partial pressure of the hydrogen chloride in the diffusate to a very low value as soon as it escapes from the walls of the diffusion tubes, and since otherwise a back diffusion will greatly lower the efficiency of the process.

A 20-liter bottle (1), with a tall dropping head, serves as a generator for the first diffusion. Six liters of *c. p.* hydrochloric acid is introduced into this bottle through the dropping funnel (2). For each 6 liters of this acid about 8 liters of conc. *c. p.* sulfuric acid is dropped into it from a very wide 24-liter supply bottle (3). The flow of acid after it is started, is controlled by the 3-way stopcock, (4), the supply being sufficient to run for 23 hours. By refilling the generator at about 4.00 P.M. each day, a very steady flow of gas is secured through the night, the regulation requiring no attention between 10.00 P.M. and 7.30 A.M. When the speed of generation begins to fall in the morning, the generator is heated to 50° by means of an air-bath heated on an electric hot plate. By this means 75% of the hydrochloric acid in the original acid can be



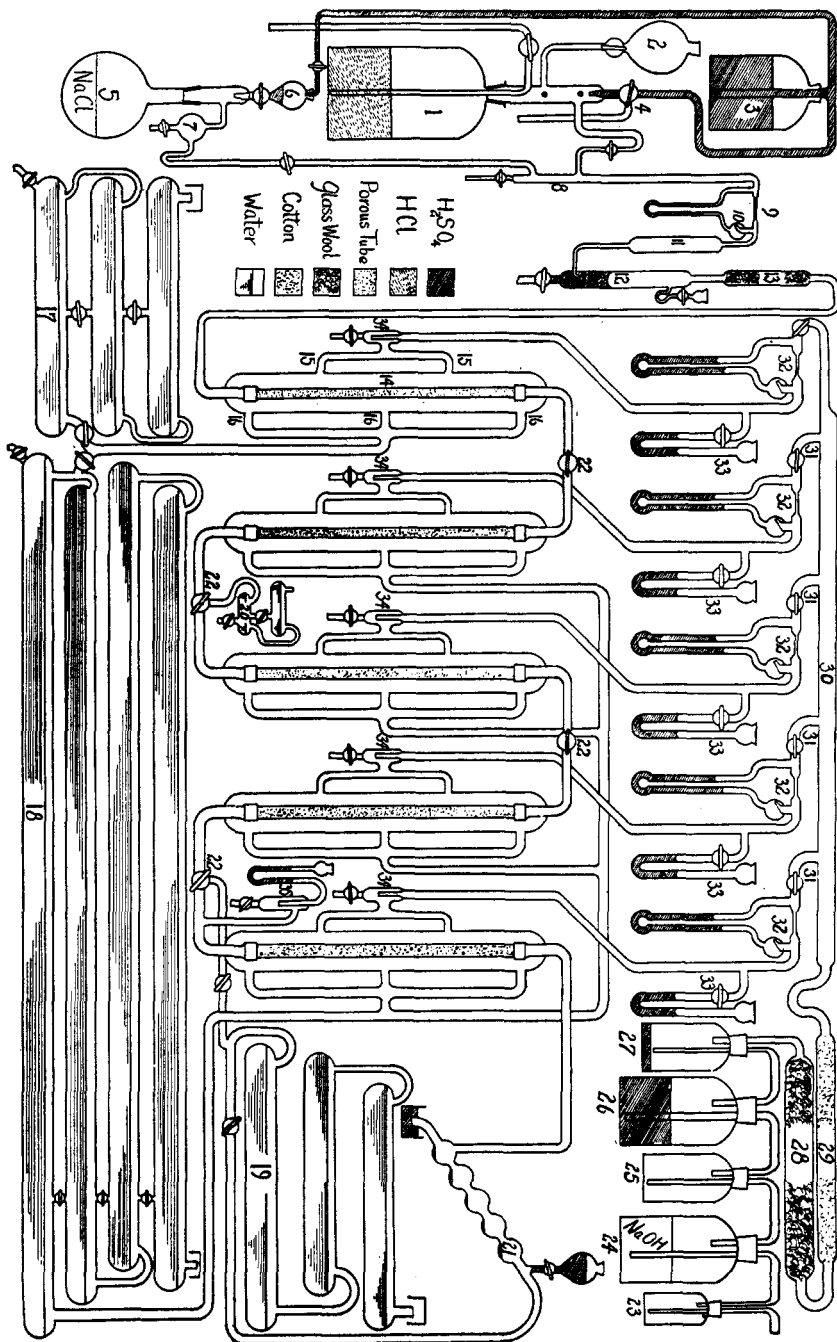


Fig. 1.

recovered. The generator is emptied by means of pressure through the siphon (4) directly into a carboy. For all succeeding diffusions the gas is generated in a 2-liter or a still smaller flask (5) into which sulfuric acid is dropped from a funnel (6). When the speed of evolution of gas from this generator falls, it is heated to 100°, thus giving nearly 100% recovery of the hydrogen chloride.

The trap (7) is to prevent an explosion of the generator, which otherwise is likely to occur if the generator happens to foam over, since the warm sulfuric acid solution of sodium hydrogen sulfate will solidify very quickly when it reaches the cold tubes. This usually clogs the tubes, and an explosion is apt to result, but has never occurred when the trap is in the system.

From the generators the hydrogen chloride passes into the trap (8) which collects moisture and sulfuric acid spray and through the flowmeter (9). Sulfuric acid is used as the manometer liquid in all of the flowmeters, and its injection into the apparatus is prevented by the traps (10). The bulb (11) is used to prevent sulfuric acid from being drawn back into the flowmeter (10) from the gas dryer (12). The thistle tube and its connections on (12) served to introduce fresh acid into the dryer, and also as a manometer to measure the pressure at the generator end of the diffusion train. The drying acid in (12) is renewed every second day. The bulb (13) is filled with glass wool, tightly packed, to filter out all sulfuric acid spray from the dried gas. After passing this the gas goes directly into the first diffusion tube (14). The first diffusion tubes are the stems of churchwarden pipes, while the succeeding ones were especially prepared for our use by the Ceramics Division of the Bureau of Standards. The latter are one meter long, 11 mm. outside diameter, with 2 mm. walls. They are sealed into glass tubes of almost the same diameter by the use of plaster of Paris. The diffusion tubes were then sealed into glass jackets 1.5 meters long, and 5 cm. in diameter. The air for sweeping out the diffusate enters the jackets through the two tubes (15) and passes out of it through the three tubes (16). These three exit tubes for each jacket are assembled into a single line leading to the absorbers for the light fraction. During the first diffusion the material from the first diffusion unit is absorbed in distilled water in absorber (17) and is designated as the light fraction from the first diffusion. During later diffusions of the heavy fraction this absorber is shunted out of the line, since its capacity is too great. The diffusate from the succeeding 4 jackets is absorbed in the large absorber (18) and when the concentration of the solution reaches 6 *N*, it is turned back into the stock of the laboratory (not, however, for any diffusion after the first) as dil. chemically pure hydrochloric acid. It is free from sulfites, sulfates, organic matter, and gives no test for iodine or bromine. The heavy fraction, or that which remains inside of the tubes at the end of the fifth or last unit, is absorbed in the absorber (19).

In the third and fourth diffusions only the first two units are used, and the small absorber (20) is used for the heavy fraction. Very large 3-way stopcocks (22) are between each two diffusion units, so that the apparatus may be used as two or more separate diffusion trains. The series of bulbs and the dropping funnel (21) constitute a sulfuric acid dryer for the heavy fraction passing from the fifth unit to the absorber (19), its purpose being to prevent any moisture from the absorber from reaching the porous tubes. The absorbers were all made on the same plan, and consist of two or more horizontal, and usually very large, glass tubes, arranged one above the other. Each of these tubes is provided with a gas inlet tube at one end, and an outlet tube at the other, and also with a tube and stopcock for allowing the acid to be dropped into the next unit below, or, on the bottom or first unit, for drawing it off from the apparatus.

The horizontal tubes are filled nearly full of pure distilled water thus leaving a long narrow passage for the gas. Nearly all of the hydrogen chloride is absorbed in the first unit, and none of this gas can be detected by the odor at the exit from the last tube.

When the solution in the first or bottom tube reaches 6*N* in concentration, it is drawn off, the solution in each of the other tubes is dropped into the tube just below it, and distilled water is poured into the last or uppermost tube. This change can be made during the operation of the apparatus, while the method of surface absorption makes it possible to keep the pressure in the tubes very close to that of the external atmosphere, and to balance properly the pressures inside and outside the tubes, so that no capillary transpiration may occur.

The air supply for sweeping out the diffusate from the jackets comes from the compressed air supply of the laboratory, and is passed into an empty bottle (23) for settling out impurities, then through 30% caustic soda solution in the very large bottle (24), through the safety bottle (25), through conc. sulfuric acid in a very large bottle (26), and is then blown on the surface of conc. sulfuric acid in the bottle (27). It is then filtered through a foot of glass wool (28) and a foot of absorbent cotton (29), and passes into the distribution line (30). From this it flows through individual stopcocks (31), through flowmeters (32), past sulfuric acid manometers (33), through traps (34) into the jackets of each unit. The traps are used to prevent sulfuric acid from getting into the diffusion units from the manometers or flowmeters. The manometer (35) and that at (12) serve to give the gas pressure in the diffusion line, while those designated as (33) indicate that in the jackets.

Air is passed through each jacket at the rate of 3 liters per minute. During the first diffusion hydrogen chloride passes flowmeter (9) at the rate of 600 cc. per minute, and at this rate  $\frac{1}{30}$  of it arrives at the absorber for the heavy fraction (19) and is collected there. For the second diffusion gas is generated at the same rate, but only four of the units are used. This gives a cut of 20. Third diffusions are run with only the first two units, gas being generated at the rate of 200 cc. per minute, and again a cut of 20 results. The total cut  $30 \times 20 \times 20$ , or 12,000, should, according to the Rayleigh theory, give an atomic weight for the chlorine in the heavy fraction of 35.54, but it is hardly to be expected that an efficiency of 100% in terms of this theory can be obtained, except possibly in a vacuum diffusion, under ideal conditions.

The heavy fraction from each diffusion is neutralized with very pure sodium hydrogen carbonate, and is used in the generator which uses salt (5) for the regeneration of the hydrogen chloride. It is found that the generation from sodium chloride occurs at a more uniform rate if carried out at a temperature of 80° until the charge is nearly spent, when the temperature is rapidly raised to 100°. If the generator at the middle of the run is giving off gas at the rate of over 300 cc. per minute, the salt cake will adhere to the bottom of the flask, until enough sulfuric acid has been run in to float it. Just as it comes loose from the bottom of the flask there is a violent evolution of gas. At rates below 300 cc. per minute the cake is gradually wetted throughout with sulfuric acid and the difficulty is avoided.

It is evident that the process of diffusion may be carried out fractionally and this was done. Thus the light fraction from the second diffusion has nearly as high a density as the heavy fraction from the first diffusion, so it is not rejected, but is rediffused, and the heavy fraction which results has nearly as high a density as that of the original second diffusion.

#### Method of Analysis and Calculation of Results.

In order to be able to determine the effects of the successive diffusions it is important to develop a method of determining with considerable precision the change of atomic weight produced. It was found that such

a method could be devised easily provided a simple and seemingly accurate hypothesis is adopted as its basis. This is that isotopes have so nearly the same atomic volumes and the same chemical properties, that no error of sufficient magnitude to affect the analyses will be introduced if it is assumed that they are exactly alike in these respects. That the isotopes of lead have the same volume within the limits of the experimental error has been shown by Soddy<sup>11</sup> and by Richards<sup>12</sup> and that their identity in chemical properties is almost complete is shown by a joint investigation by Gale, Aronberg, and one of the writers;<sup>13</sup> since they found that the difference in the wave length of the line  $\lambda 4058$  caused by a difference of about 0.9 in the atomic weight, was only one-millionth of the wave length. The difference in chemical properties between these isotopes may be expected to be very small. This discovery has been confirmed by Merton.<sup>11</sup> However, even though this hypothesis is used as a basis for calculation, the proof that a *separation* of the two isotopes of chlorine has been made is *entirely independent* of the assumption, since no differences of atomic volume could be detected unless a separation had first been effected.

The simplest method for determining the increase of atomic weight was thought to be the determination of the densities of specimens of highly purified ordinary hydrochloric acid, and a comparison with these of the density of a specimen of acid produced by diffusion. This will be termed the isotopic acid, and the plan was to fix the molecular concentrations of these two acids as determined by titration, at the same value, and to compare the weights of hydrogen chloride which they contain. It is evident that the weight of the isotopic acid should be greater than that of the ordinary or "comparison" acid, since the present article refers to the heavy fraction. These weights are in the same ratio as the formula weights of hydrogen chloride in the two solutions, so

$$\text{and} \quad M_i = 36.468 \cdot W_i/W_c \quad (13)$$

$$\text{or} \quad A_i = M_i - 1.008 \quad (14)$$

$$\Delta A = 36.468 \Delta W/W_c \quad (15)$$

Here  $M_i$  and  $A_i$  are the molecular weight of hydrogen chloride and the atomic weight of chlorine, respectively,  $W_i$  and  $W_c$  are the weights in grams of the hydrogen chloride in the same volumes (*e. g.*, pycnometer full) of the comparison and the isotopic acids, and  $\Delta W$  is the increase in weight which occurs when the isotopic acid is substituted for the comparison acid. Equation 15 gives the most accurate results, since it does not

<sup>11</sup> Soddy, *Nature*, **94**, 615 (1915).

<sup>12</sup> Richards, *THIS JOURNAL*, **38**, 221 (1916); and "Presidential Address to the American Association for the Advancement of Science," 1918.

<sup>13</sup> Harkins and Aronberg, *Proc. Nat. Acad. Sci.*, **3**, 710-15 (1917); *THIS JOURNAL*, **42**, 1328-35 (1920); Aronberg, *Astrophys. J.*, **47**, 96-103 (1918); Merton, *Proc. Roy. Soc. London*, **96A**, 388-95 (1920).

involve an exact knowledge of the weight in solution of either the comparison or the isotopic acid, but only a precise value for the increase in weight. The thermostat should be regulated to  $0.001^\circ$  or better, and the pycnometer should consist of a large spherical bulb with a short but very narrow neck graduated with a very fine line at its narrowest point. Above the neck is a bulb large enough to hold any solution which rises through the neck on account of thermal expansion. This is fitted with a very close fitting ground-glass stopper, and with very fine tubes for filling and emptying. The pycnometer is preferably made of quartz, and the tubes of platinum or hard gold.

While the above procedure is the simpler from the standpoint of the equations involved, it happens that another method is more economical of time and material, so what has actually been done in most of the cases is to adjust the comparison and the isotopic acids to the same density, and to determine the number of molecules of hydrogen chloride, and therefore the number of atoms of chlorine, present by titration. In this case the acid in the pycnometer has a higher molecular concentration when the comparison acid is used. Very accurate density determinations have been made on solutions of very pure ordinary hydrochloric acid by Dull in this laboratory. From his data it may be calculated that the "apparent density" of hydrogen chloride in 5.91 *N* hydrogen chloride is 1.785, in 5.79 *N* it is 1.7852, while in 5.20 *N* it is 1.787, and in 2.315 *N* it is 1.856.

The difference in the titration values of the comparison and the isotopic acids may easily be calculated in the following way for any desired increase in the atomic weight ( $-\Delta A$ ) of chlorine. Calculate the increase of weight which would occur if the comparison acid in the pycnometer were to be replaced by isotopic acid of the same titration value. Then calculate the number of equivalents of hydrogen chloride in the isotopic acid which must be replaced by water of a density 0.997077 (or 0.99604 as weighed by brass weights in air, if the temperature of the thermostat is  $25^\circ$ ) in order to reduce its weight by the above difference. This gives the difference in the titration values of the two solutions when adjusted to the same density, which will be given directly in terms of 0.01 *N* sodium hydroxide solution, since the titration was completed with a base of this concentration, though begun with 1 *N* solution.

$$\Delta T = \frac{V \cdot N \Delta A}{1000 \cdot M_c} \cdot \frac{d\text{HCl}}{d\text{HCl} - d\text{H}_2\text{O}} \cdot \frac{1}{10^{-3}} \quad (16)$$

or

$$\Delta A = 100 \cdot \Delta T \cdot \frac{d\text{HCl} - d\text{H}_2\text{O}}{d\text{HCl}} \cdot \frac{M_c}{V \cdot N} \quad (17)$$

Here the symbols have the same meaning as before, except that the following new ones are employed:  $M_c$  is the equivalent weight of hydrogen chloride in the comparison acid, and equals 36.468 in the present experi-

ments;  $N$  is the normality of the comparison acid;  $d\text{HCl}$  is the apparent density of hydrogen chloride in the comparison acid;  $d\text{H}_2\text{O}$  is the density of water at the same temperature;  $\Delta T$  is the difference in grams of  $1/100$  weight normal sodium hydroxide between the pycnometer full of the two acids;  $10^{-5}$  is the number of equivalents of sodium hydroxide in 1 cc. of 0.01  $N$  base.  $V$  is the volume of pycnometer in cc. If  $V$  cc. is titrated, the right hand side of the Equation (17) for  $\Delta A$  should evidently be multiplied by  $V/v$ .

Let  $T'_c$  and  $T'_i$  represent the titration values of the comparison and isotopic solutions in terms of normal solutions, then it is evident that Equation 17 may be given the following form.

$$\Delta A = \left( \frac{T'_c}{T'_i} - 1 \right) \frac{d\text{HCl} - d\text{H}_2\text{O}}{d\text{HCl}} \cdot M_c \quad (18)$$

**Method of Adjusting the Densities of the Isotopic and Comparison Acids.**—After a preliminary determination of the densities of the two solutions, the concentration of the solution was read from a graph giving concentrations in terms of the density of ordinary pure hydrogen chloride, and from these values the amount of water necessary to decrease the concentration of the more concentrated solution to that of the more dilute was calculated. This first adjustment brought the densities of the solutions sufficiently close so that a difference of 5 or 6 mg. was all that remained for a volume equal to that of the pycnometer.

A second dilution was made by adding water up to the exact amount called for by the equation  $(d_1 d_2 - d_2) W_w = W_s (d_2 d_1)$ , where  $d_1$  is the smaller, and  $d_2$  the larger density,  $W_w$  is the weight of water to be added to the weight  $W_s$  of the more dense solution in order to make the densities the same. This equation is not exact, since it takes no account of the volume change produced in adding water to approximately 6  $N$  acid, so it does not bring the two weights closer together than 0.6 mg. An exact equation could easily be developed, but even with the form used only 0.2 g. of water needed to be added to 75 g. of solution in the third dilution.

**Error of Filling.**—The pycnometer could be filled repeatedly with a *maximum* variation of 0.0012%, while the usual error was considerably less. The thermostat was constant to within less than 0.001°.

**Method of Titration.**—First a series of indicator standards was made up in 125cc. tightly glass-stoppered Erlenmeyer flasks.<sup>14</sup> In each of these was put the same volume of conductivity water and the same amount of methyl orange as was used in the titrations. To these were added in order 0, 2, 4, and 6 drops of 0.01  $N$  hydrochloric acid. The titrations

<sup>14</sup> Flasks with very narrow necks will be used for all future work, so that the evaporation may be decreased.

were ended at a color between that in the 2-drop and the 4-drop flasks, and in good daylight the effect of one drop of 0.01 *N* base could be readily detected. A 1 *N* solution of sodium hydroxide was used to carry the titration to within one drop of the end-point, when it was finished with 0.01 *N* solution of the same base. Weight burets of 60 g. capacity were used and these were weighed on a balance sensitive to 0.02 mg. It was found that the use of a heavy "vacuum" stopcock grease completely stopped all loss of weight of the burets due to evaporation of the solutions through the ground-glass stopcocks.

The samples for titration were weighed by measuring 5 cc. of the 6 *N* solution, dropping it into the flask, and then determining the weight on the same balance as that used for the pycnometer. The ground-glass stoppers in the sample flasks were kept dry during the whole determination.

**Purification of Acid.**—The acid used in the analyses as the reference or comparison acid was the light fraction from the first diffusion. A calculation showed that its atomic weight could not have been changed sufficiently to be detectable, and the process used would result in a considerable purification. The acid was treated with potassium permanganate and boiled to expel any iodine, bromine, or chlorine liberated, and was then distilled, rejecting the first third and the last one-fourth.

The isotopic acid was purified in several ways. As has been stated it was formed by the action of very pure sulfuric upon *c. p.* hydrochloric acid. The gas came in contact with only carefully cleaned and dried glass and porous porcelain, and was absorbed in conductivity water. After the second diffusion the salt formed by neutralizing the acid by very pure sodium hydrogen carbonate was recrystallized three times from pure water and was very thoroughly drained and washed with pure water each time. The mother liquor from these crystallizations showed no trace of iodine by the use of a test which would detect one part of iodine as iodide in twenty thousand parts of sodium chloride, as determined by repeated tests. This test consisted in the use of nitrosyl sulfuric acid and carbon disulfide with the proper precautions. Neither could bromine be detected in these mother liquors, but we did not rely upon this fact to insure the absence of bromine. In addition to these three crystallizations, the acid, after the third diffusion was treated with potassium permanganate and distilled using exactly the method employed with the comparison acid, except that the first and last fourths were rejected and the middle half was saved. Additional purifications were made by precipitation of sodium chloride from aqueous solution by the addition of isotopic hydrogen chloride. The sodium hydroxide used in the analyses gave no test for bromine. It was converted into sodium chloride and recrystallized, and the mother

liquor again gave no test for bromine. However, after the sodium hydroxide was added to any sample the latter was always purified carefully.

### Results.

In January, 1920, Mr. C. E. Broeker had produced about 5 g. of hydrogen chloride which was the heavy fraction given by a cut of about 8000. Shortly afterward this was increased to about 20 g. with nearly as large a cut. However, the analyses made in January by Harkins and Broeker used nothing but the original sample. The purification of the acid was made by recrystallization of sodium chloride. In purifying most of the operations are carried out before the sample has been reduced to such a small mass, but at least one purification is always carried out with the final residue. The titration values indicated increases of atomic weight of 0.052, 0.059, 0.057, 0.055, and 0.053 units of atomic weight. A second series of analyses on another sample, gave slightly higher values.

Mr. Broeker's work was interrupted by illness in April, 1920, but on account of his unusual enthusiasm and energy he continued to work for two weeks after his illness began. Since just at this time he adopted a new system of labeling, and his illness took an unexpected turn for the worse and finally resulted in his death, it happened that his records were not completed, and this resulted in some uncertainty in identifying his samples. For this reason, and for the additional purpose of demonstrating that the separation could be carried out by the use of an independent apparatus, and by using different materials, an entirely independent diffusion was started. The hydrogen chloride obtained in the present series of diffusions will be added, in the form of sodium chloride, to the sodium chloride obtained by him, as soon as the atomic weight has increased by the amount given above.

It should be realized that in work of this kind it is not merely the increase in atomic weight which counts, but also the amount of material which is obtained, since the future progress of the work, and also the extent to which the material can be purified, depends largely upon the amount of material available. While the rise in atomic weight obtained in the independent series of diffusions carried out this year, is not large, it seems to be definite, and of the order of magnitude to be expected from the earlier results given above, so a report of progress will be given.

**Analysis of the Purified Third Diffusion Residue (Cut = 12,000).—**In order that the magnitude of the errors involved may be realized the actual data for some of the analyses will be presented. First the reference acid and the isotopic acid were adjusted to practically the same density in a Harkins' pycnometer of about 22cc. volume. The weights were as follows:



## ANALYSES.

	First Series.		Second Series (after another distillation).	
	Reference acid.	Isotopic acid. ( $t=25^{\circ}\pm 0.0005^{\circ}$ )	Reference acid.	Isotopic acid.
1.	37.2533	37.2530	37.2100	37.2095
2.	37.2535	37.2527	37.2100	37.2098
Av.	37.2534	37.25285	37.2100	37.20965
Diff.	0.00055 g. = 0.00148%		0.00045 g. = 0.00121%	

TABLE II.

## DATA ON THE ATOMIC WEIGHT DETERMINATIONS.

Note that the two columns on the left of the table refer to one set of analyses, the two on the right to a second series.

No. of mols. of HCl in 100 g. of sol.; from density.	First Series. $N = 5.91.$	Second Series. $N = 5.79.$
Density of Isotopic Acid.	1.10195	1.00983

Bar. Pressure = 748.4 mm. ( $h = 7.17$ )<sup>a</sup> to 746.5 mm.  
( $h = 10.4$ ).  $t = 24^{\circ}$  to  $26^{\circ}$ .

Wt. of pycnometer of water. 35.0350  
" " " 13.2765

DATA FOR THE TITRATION OF THE REFERENCE AND ISOTOPIC ACIDS.<sup>b</sup>

	First Series. NaOH used per 5 g. of acid.	Second Series.
26.2613	26.1970	25.7887
26.2669	26.2004	25.7848
Av.	26.1987	25.7867
Diff. (g. of 0.01 N NaOH)	6.54	7.07

After standing for one day.

26.2630	26.2030	25.7755	25.7094
26.2673	26.2069	25.7745	25.7064
	26.2030	25.7752	
Av.	26.2043	25.7751	25.7079
Diff. (g. of 0.01 N NaOH)	6.08		6.72

After standing for two days.

		25.7695	25.7045
		25.7671	25.7002
	Av.	25.7688	25.7023
Diff. (g. of 0.01 N NaOH)			6.65

<sup>a</sup> and <sup>b</sup>—For footnotes see next page.

Increase of Atomic Weight.						
	First Series.			Second Series.		
	Uncorr.	Correction for density.	At. wt. increase	Uncorr.	Correction for density.	At. wt. increase.
1st. set.	0.0356	-0.0018	0.0338	0.0393	0.0016	0.0377
2nd. set.	0.0331	-0.0017	0.0312	0.0374	0.0015	0.0359
3rd. set.				0.0370	0.0016	0.0354
			-----			-----
Av. increase in at. wt.			0.0325			0.0363
Average of Series 1 and 2			0.0344			

100 g. of chlorine obtained of atomic weight 35.494.

<sup>a</sup> The absolute humidity in mm. of mercury is represented by *h*.

<sup>b</sup> The weights of base and acid used in these titrations are reduced to the same barometric pressure and the same humidity for each series.

The corrections of about 0.0018 for the results of the first, and of 0.0016 for the results of the second series were calculated from the density differences by means of the same equation as was used for the calculation of the results of the titrations.

The difference between the averages of the atomic weights for the first and second series of analyses is 0.0038 units of atomic weight which is very near the possible error in the atomic weight of chlorine according to Richards. While the data given indicate that the comparison method described is a very accurate one for the determination of the atomic weight of an isotope of chlorine, our experience has shown that its precision may be increased, provided as large quantities of acid are available, by the observance of certain precautions which may be introduced. The atomic weight of the chlorine produced by diffusion by the writers is very close to 35.494, while that obtained by Harkins and Broecker was 35.515. However, the amount of material produced by the present work is very much greater, since a few days more of diffusion will give about 100 g. of acid with this atomic weight for the chlorine. Since the efficiency of the process as conducted has not proved to be very high in terms of the Rayleigh diffusion theory, it is planned to conduct the rest of the diffusions upon the smaller portions now on hand, by a vacuum system of diffusion, which should give a high efficiency. The apparatus which is to be used will be described in the next report, and will be similar in many respects to that developed in this laboratory by Dr. Turner for the diffusion of chlorine. Since the amounts of material to be handled are now greatly reduced a further increase of from 0.05 to 0.1 units in addition to that already secured should be obtained quite rapidly, but the rapidity of increase will be dependent upon the amount of the material secured, since a small increase with a large yield of material may be more difficult to secure than a larger increase on a small amount of material.

**Repurified Fourth Diffusion Residue** (Cut = 240,000).<sup>15</sup>—The hydrochloric acid obtained from the third diffusion had been converted largely into sodium chloride in the titrations on the third diffusion residue, so the remaining acid was neutralized with sodium hydrogen carbonate. The salt thus obtained was converted into hydrogen chloride, and again diffused. The hydrochloric acid thus obtained was distilled fractionally, after heating with potassium permanganate. The middle portion was used for the analyses reported below.

## ANALYSES.

	Weight <i>in vacuo</i> of pycnometer plus	
	Reference acid. ( <i>t</i> , 25° + 0.0005).	Isotopic acid.
1.	36.4461	36.4465
2.	36.4460	36.4465
Av.	36.44605	Diff. 0.00045
No. mols. in 1000 g. solution from density.		Density of isotopic acid.
	<i>N</i> = 5.22	<i>d</i> <sup>25</sup> = 1.08868
Barometric pressure = 737 to 739 mm. Absolute humidity = 7.6 to 7.05 mm. Temperature = 24 to 26°.		

Data for the Titration of the Reference and Isotopic Acids.  
(All weights corrected to 737 mm. and *h* = 7.6.)

*N* NaOH per 5 g. of acid.

Reference acid.	First Day.	Isotopic acid.
G.		G.
23.3430		23.2898
23.3456		23.2870
<hr/>		<hr/>
23.3443		23.2884
Diff. 5.59 g. of 0.01 <i>N</i> NaOH.		
	Second Day.	
23.3359		23.2793
23.3401		23.2785
23.3369		23.2755
<hr/>		<hr/>
23.3376		23.2778

Diff. 5.98 g. of 0.01 *N* NaOH.

Increase in Atomic Weight above 35.46.

	Uncorr.	Correction for density.	Atomic weight increase.
1st. day's determinations	0.0346	Add. 0.0017	0.0363
2nd. day's determinations	0.0370	0.0017	0.0387
			Av. 0.0375

Nine g. of chlorine of atomic weight 35.498 was obtained in this diffusion. The fourth diffusion was not so efficient as the first three, since the

<sup>15</sup> Report added to paper on May 16, 1921. Determinations by Anson Hayes and S. K. Allison.

apparatus is better designed for larger samples, and in this diffusion the gas passed through only a short length of porous tube of large diameter.

### Result of Additional Purifications.<sup>16</sup>

As has been stated, all of the acid used in this series of determinations was purified after the second diffusion by conversion into sodium chloride through neutralization with very pure sodium hydrogen carbonate, and by three successive fractional crystallizations from pure water. The highly concentrated *mother liquor* from all of these crystallizations, after removing a part of the salt content, gave no test for iodine or bromine. The hydrochloric acid obtained from this salt was, nevertheless, heated with potassium permanganate, and fractionally distilled.

In order to remove all possible doubt in regard to the presence of such impurities, it seemed advisable to make still further purifications. However, this could not be done successfully, using the methods developed for this work, on the 9g. sample of the fourth diffusion residue, since the purification involves the rejection of the greater part of the acid used. The sample was therefore obtained largely by diffusing the *light* fraction from the third diffusion, and adding the considerable quantity of acid thus obtained to the fourth diffusion residue. Since the fourth diffusion had not proved very efficient, the sample thus obtained should have an atomic weight not far from that obtained in the third diffusion residue.

The acid obtained in this way was heated with potassium permanganate and distilled fractionally. The middle portion was neutralized with very pure sodium hydrogen carbonate. Part of the salt thus obtained was then dissolved in 35 cc. of conductivity water, and precipitated by passing in hydrogen chloride generated from the remainder of the isotopic sodium chloride. This purified salt after the hydrochloric acid had been drained off thoroughly was again separated into two portions, and the process was repeated. The apparatus used was wholly of glass.

The 9 g. of sodium chloride thus obtained was carefully separated from the considerable amount of liquid, and the acid still remaining on the salt was driven off by heating in platinum to 300°. The salt was again converted into hydrochloric acid, and was then distilled fractionally. The distillate was again redistilled, and the resulting isotopic acid used in the determinations.

The comparison acid used was subjected to exactly the same set of purifications and treatment using the same apparatus and the same materials, the only difference being that it had not been subjected to the diffusion process. The density determinations and the analyses are given herewith.

<sup>16</sup> Atomic weight determination by Anson Hayes and S. K. Allison. Report added June 9, 1921.

## ANALYSES.

	Reference Acid.	Weight <i>in vacuo</i> of pycnometer plus ( $t = 25^\circ \pm 0.0005$ ).	Isotopic Acid.
1.	50.8133		50.8134
2.	50.8136		50.8134
	<hr/>		<hr/>
	50.81345		50.8134
	Diff. 0.00005 g.		

No. of mols in 1000 g. from density.

 $N$  2.315

Density of isotopic acid.

 $d = 1.037855$ Barometric pressure 754 mm. ( $h = 9.82$  mm.),  $t = 22.4^\circ$  in balance.

Data for the Titration of the Reference and Isotopic Acids.

(All weights corrected to 754 mm. and  $h = 9.82$  mm.) $N$  NaOH per 10 g. of acid.

Reference Acid.	Isotopic Acid.
G.	G.
19.6369	
19.6363	19.5940
19.6399	
<hr/>	
19.6377	

Diff. = 4.37 cc. of 0.01  $N$  NaOH.

Increase in atomic weight above 45.46

0.0318

Atomic Weight = 35.4918

While the above results are all that were obtained under the best conditions on this particular sample, since the other samples were of necessity allowed to stand overnight, two additional titrations of the isotope were then obtained as follows: 19.5974, and 19.6001 g. of  $N$  NaOH to titrate 10 g. of isotopic acid. These confirmed the result obtained above as to its general magnitude, but gave a determination which was slightly more in error. It had been found that under the conditions under which these samples stood, the titration value is very slightly increased, so the atomic weight obtained, from these two titrations, 35.4886, is probably too low. The atomic weight determination for this series is slightly less accurate than for the three preceding series, as the amount of material used was less.

## Summary.

1. A definite increase in the atomic weight of chlorine has been obtained in experiments conducted in this laboratory by the diffusion of hydrogen chloride at atmospheric pressure. The increase in atomic weight amounts in different experiments to from slightly less than to considerably more than one part in a thousand (1 in 645). The amount of separation obtained is in a certain sense considerably more than might be supposed from this figure, since a considerable amount of this isotopic acid has been produced. This seems to be the first separation of isotopes reported from which there is any definite evidence.

2. The separation of isotopes by diffusion is discussed in terms of the Rayleigh diffusion equation, which applies to a diffusion into a vacuum. It is indicated that for a high efficiency the pressure of the gas on both sides of the diffusion wall should be low, first in order to secure good mixing, and second to insure that the passage through the porous partition shall be entirely molecular. Since the large amounts of acid used in the preliminary diffusions have now been largely reduced, the further work in this laboratory will be carried out at low pressures, and with porous material in which the pores are very small.

3. A method which is at the same time very precise and very rapid has been devised for the determination of the atomic weight of any isotopic form of chlorine.

4. It is found that in the separation of isotopes the percentages present of the different isotopes are as important factors as the atomic weight differences. Thus, contrary to what has been supposed, it is shown, even aside from the greater difficulties involved in obtaining and handling neon, that it is easier in terms of the cut necessary to produce a small increase in the atomic weight of chlorine (of the magnitude of 0.05 units) than to produce the same increase in the atomic weight of neon.

5. In January, 1920, Harkins and Broeker had separated 5 g. of isotopic chlorine (in the form of hydrogen chloride) of an atomic weight 35.515. Preliminary notices of this separation were published in the February, 1920, number of the *Physical Review*, in *Science*, and in *Nature*. The present research was begun in order to confirm the earlier work, in June 1920, and has thus far used none of the material left by Mr. Broeker at the time of his death in April 1920. An apparatus of higher capacity, but somewhat lower percentage efficiency, has been used. Nine g. of chlorine of atomic weight 35.498, and 90 g. of atomic weight 35.494, have been obtained, the atomic weight results having been determined upon very highly purified material. In addition to this considerable isotopic chlorine of lower atomic weight has been obtained, about 400 g., whose atomic weight has not been determined, but should be more than 0.02 units higher, and 4 kg., whose atomic weight should be more than 0.01 unit higher, than for normal chlorine, judging from the efficiency of the whole process. Dr. W. D. Turner prepared several kg. of this last grade in the summer of 1918, and about 20 g. of much more highly diffused chlorine in 1916-7, but the atomic weight work was left incomplete on account of the war. A notice of the beginning of this work was published in THIS JOURNAL in January, 1916. In 1915, definite evidence based upon atomic weight relations was presented by one of the writers that chlorine consists of isotopes. An important feature of the present investigation is that it was begun four years before any entirely direct experiments had proved the existence of isotopes in chlorine, and a

notice of the separation was published only two months after Aston's preliminary notice in regard to their existence.

The writers wish to express their indebtedness to the C. M. Warren Fund of the American Academy of Arts and Sciences for a grant of five hundred dollars to be used in carrying on the present investigation. A part of this has been used in the purchase of an analytical balance sensitive (for a  $\frac{1}{2}$  mm. deflection) to  $\frac{1}{100}$  mg. to be used in weighing small samples of higher or lower atomic weight. Thanks are also due to the Wolcott Gibbs Fund of the National Academy of Sciences for a similar grant to be used in determining the effects of radiation and high temperatures upon the stability of the nucleus of the atom, and also for positive ray work upon isotopes. We wish to thank the Grasselli Chemical Company of Cleveland, Ohio, and the Mallinckrodt Chemical Company of St. Louis for gifts of considerable amounts of hydrochloric and sulfuric acids; the Jaques Mfg. Co. for a barrel of sodium hydrogen carbonate which proved to be purer than the "analyzed" material previously purchased; Dr. F. L. Dunlap for his assistance in securing material; T. H. Liggett and S. K. Allison for assistance in the experimental work; and the Bureau of Standards and the Coors Porcelain Company for the preparation of tubes of different porosities.

Diffusions on the light fraction were carried out by C. E. Broeker in the year 1919-20, and the results of this work will be reported in a later paper. It is hoped that funds for the construction of a centrifugal machine may be secured, as it seems probable that the centrifugal method, or at least some method other than those of diffusion, thermal diffusion, or vaporization at low pressures, must be used if a separation of any considerable magnitude is to be obtained without the expenditure of an unreasonable amount of effort.

CHICAGO, ILL.