2. It has been shown that the constancy of the steady-state function for this catalytic reaction can be greatly improved by substituting activities for the concentrations of all electrolytes involved. The average value of the steady-state function, so corrected, is 1.7.

BERKELEY, CALIFORNIA

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

THE SEPARATION OF THE ELEMENT CHLORINE INTO ISOTOPES. THE LIGHT FRACTION

BY WILLIAM D. HARKINS AND FRANCIS A. JENKINS

RECEIVED AUGUST 14, 1925 PUBLISHED JANUARY 8, 1926

1. Introduction

In January, 1920 Harkins and Broeker[1] *obtained the largest separation* of the isotopes of chlorine thus far reported. They obtained about 10 g. of chlorine of atomic weight 35.515, that is, with an atomic weight 0.058 higher than that of the ordinary element. Two other separations of the heavy fraction from chlorine[2] have been reported from this Laboratory. The present paper describes the results of a series of diffusions of hydrogen chloride through the stems of church-warden smoking pipes at atmospheric pressure. The diffusions were carried out in such a way as to obtain chlorine which has a lower atomic weight than the ordinary element. The decrease in atomic weight amounted to 0.039 unit. Thus the total extreme separation thus far obtained in this Laboratory amounts to 0.097 unit, *or one part in 365*. This is the greatest relative difference in atomic weight obtained by artificial means for any element.

2. *Experimental Part*

Construction and Operation of the Apparatus.—The tubes used to give a porous wall for the diffusion were the stems of church-warden pipes made in Scotland, since these had been found to have finer pores than any of the other porous porcelain available. They were carefully selected from the pipestems used in similar earlier work in this Laboratory. They had an average inside diameter of 2.0 mm. and a wall thickness of 2.2 mm. The small inside diameter aids in securing a thorough mixing of the gas.

Great care was taken in the selection of the tubes to insure absence of small leaks, and to obtain the proper degree of porosity. One end of the tube under investigation was first tightly closed with sealing wax and the other connected to an air pressure line and a manometer. The pipestem was then inserted in a glass jacket provided with an exit connected with a device for measuring the rate of efflux of the air. The air pressure was then regulated so that the manometer indicated an excess of 20 cm. inside the tube, and the velocity of diffusion of air into the jacket was measured, keeping the pressure

---

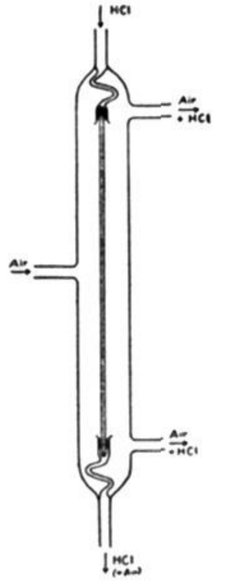
[1] Harkins and Broeker, *Science*, **51**, 289 (1920); *Phys. Rev.*, **15**, 74 (1920); *Nature*, **105**, 230 (1920).

[2] Harkins and Hayes, THIS JOURNAL, **43**, 1803 (1921). Harkins and Liggett, *J. Phys. Chem.*, **28**, 74 (1924).

in the latter at one atmosphere. Of 82 pipestems thus tested, 24 were chosen whose diffusion rate was neither exceptionally high nor low. They had an average length of 40 cm., and the diffusion rate was of the order of 2.5 cc. per minute, per 10 cm. of length.

With these tubes, several units of Type A (Fig. 1) were constructed. Plaster of Paris served to seal the ends of the pipestems tightly into glass tubes, and leaks were prevented with a small amount of paraffin. The short coils were used to reduce any strains that might result on cooling the glass seals, since such strains might loosen the plaster-of-Paris joint. A test of the diffusion rate was repeated for each completed unit, to insure the absence of leaks.

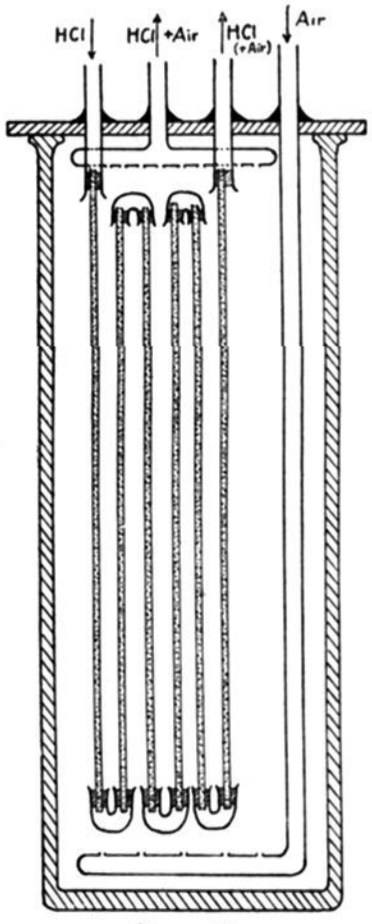
Trials showed that when six such units were connected so that hydrogen chloride passed in series through the pipestems, a cut of approximately 2 was obtained. The method of generating the hydrogen chloride, and of sweeping out and collecting the diffused gases was similar to that used in work on the heavy fraction, and has been fully described.[2] Capillary flowmeters permitted the regulation of the rate of flow of hydrogen chloride at 100 cc. per minute, the rate required to produce the desired cut of 2. This corresponds to a linear velocity of about 40 cm. per second for the gas in the pipestems. The air used for sweeping out the light fraction was purified as recommended by Harkins and Hayes, and was passed into each jacket at the rate of 1 liter per minute. Both fractions were absorbed in the surface of conductivity water in absorbers of 1-liter capacity, four of these being required in the case of the light fraction. Glass seals were used for all connections.



Type A.
Fig. 1A.—Diffusion unit.

To increase the capacity of this apparatus, an exactly similar train of 6 Type A units was connected to the same hydrogen chloride generator, and arranged so that the fractions could be collected in the same sets of absorbers mentioned above.

In work in this Laboratory on the heavy fraction, very large cuts were made in a single operation. It is evident that the necessity of using smaller cuts for the light fraction greatly increases the number of individual diffusions which must be made in order to obtain the same change in molecular weight. In view of this fact, and also of the necessarily slow rate of gas flow, it was decided to construct another independent apparatus, utilizing units of Type B (Fig. 1). These differed from the other type in that all of the pipestems of one series were in a single jacket. The latter was a large glass cylinder, closed at the top with a piece of plate glass, through which holes were bored to admit the tubes conducting the gases, and which was tightly sealed to the cylinder with paraffin. Sealing wax served to hold the tubes in position, and to render the apparatus air-tight. The slight inferiority of this type as regards the efficiency of the sweep-out was later found to be negligible. The second apparatus comprised two of these units connected to another generator for hydrogen chloride and arranged so that the air, which entered each at the rate of 6 liters per minute, swept the light fractions into the same set of absorbers.



Type B.
Fig. 1B.—Diffusion unit.

Since it is advisable, in a gaseous diffusion of this sort, to maintain the total pressure in the jackets slightly higher than that inside the porous tubes, small sulfuric acid manometers were connected to the hydrogen chloride line at the beginning of each diffusion train. Others were sealed to the tubes conducting the air, adjacent to the jackets. During the diffusion, a glass cover over the air exit of the light fraction absorbers was so adjusted that the air pressure in the jackets was a few millimeters higher than the pressure of the hydrogen chloride at the beginning of the train, which was obviously its highest value.

The object of the above-mentioned pressure difference, as pointed out by Mulliken and Harkins,[3] is to reduce any mass motion of the gases through the porous wall to a minimum. The inherent mass motion, due to the unequal rates of diffusion of the two gases in opposite directions, would be reduced by having the hydrogen chloride diffuse against a slight positive pressure difference. With such a difference, mass motion would be much larger if leaks were present. Another test to insure the absence of accidental leaks was carried out on each completed series of pipestems, the rate of diffusion of air under a given pressure difference usually being only slightly higher than that to be expected from the values for the individual tubes. That the mass motion was not large was further proved by conducting two trial diffusions, one in which the air pressure in the jackets was rather high (10 cm. of sulfuric acid), and another in which it was as low as possible (0.5 cm.). The cut, as determined by titration of the acids, remained the same within the experimental error of the determination.

Diffusions.—The first diffusion was effected entirely with the apparatus consisting of Type A units. Hydrogen chloride was produced by the interaction of chemically pure hydrochloric and sulfuric acids, using the generator described by Harkins and Hayes,[2] which renders the process semi-automatic. Sufficient hydrochloric acid was introduced to produce the gas at the required rate (200 cc. per minute), for 23 hours, and the rate of flow maintained practically constant throughout the period by occasional adjustment. Before it passed into the pipestems, the hydrogen chloride was dried by a sulfuric acid column filled with glass beads, and was then completely freed from spray by passage through 1 meter of tightly-packed glass wool.

Twelve kg. of the gas was thus diffused by practically continuous operation for two months. Whenever the concentration of the acid in the lower absorbers reached 6 *N*, it was drawn off and neutralized with sodium hydrogen carbonate of the same high grade of purity as that used in previous work on this problem. The sodium chloride from the light fraction, obtained by evaporation, was dried and reserved for the succeeding diffusion. The material from any of the runs in which variations in the rate of flow, or other disturbing factors, had entered was united to form another sample, for a purpose described below.

---

[3] Mulliken and Harkins, THIS JOURNAL, **44**, 38 (1922).

The light fraction from the first diffusion yielded 9.8 kg. of sodium chloride. This was used as the source of hydrogen chloride for the second diffusion. Sulfuric acid was dropped on the salt in a one-liter flask, connected to the system by a ground joint, and warmed by a water-bath to 80°, or to a higher temperature near the end of the run. A fairly constant evolution of gas may, with some practice, be obtained in this way. For this diffusion, both types of apparatus were employed, approximately half the material going into the operation of each. In order to determine whether the units of Type B gave as high an efficiency as those of the A type, and to avoid losses of efficiency due to mixing fractions of different value, the light fraction from these units was kept separate after the second diffusion. The following diffusions were thus made entirely independently, utilizing, in the two different types of apparatus, the approximately equal quantities obtained as the light fractions from the second diffusion. This procedure was followed until the preliminary atomic-weight comparisons were made, so that the result was essentially two independent separations. The hydrogen chloride diffused in the units of Type A will be designated as "Material I," and that from the other apparatus, "Material II." For the determination of the optimum working efficiencies of each apparatus, the method mentioned above of segregating all material from runs which were in the slightest degree unsatisfactory was used. This material constituted a third sample which continually increased in quantity, and was subjected to diffusion in both types of apparatus. It will later be referred to as "Material III."

Approximately 250 g. of sodium chloride in each apparatus served to generate the gas at the required rate for 6 to 7 hours. Forty of these runs comprised the second diffusion, and gave 4.32 kg. of sodium chloride as the light fraction, for use in the third diffusion. A slight loss of material at the end of each run was unavoidable, since a certain minimum quantity of salt was necessary to maintain the evolution of the gas at the necessary rate.

Six such diffusions, with a cut of very nearly 2, were first carried out, each time the heavier fraction being set aside. The sixth diffusate designated as A6 (Fig. 2) contained about 200 g. of sodium chloride, divided into the three samples mentioned above. These were subjected to purifications, and were analyzed separately in such a way as to permit determinations of their atomic weights, by methods to be described later.

Several determinations of the cut, made during the initial diffusions by titrating samples of the heavy and light fractions, gave values closely approximating 2.00, never differing by more than 5%. The apparatus with Type A units usually gave a slightly lower value, varying from 1.94 to 1.90. This was corrected by decreasing the initial rate of flow of hydrogen chloride to 90 cc. per minute in each diffusion train. Slight.

unavoidable fluctuations in the rate make it impossible to adjust the cut exactly. Variations of a systematic character were noticed, however, the cut decreasing on long-continued diffusion. Such an effect could only be ascribed to a slight increase in the apparent porosity of the tubes on thorough drying.

After the completion of the atomic-weight comparisons on Fraction A6, the diffusions were continued, fractions of the same value being united according to the scheme indicated in Fig. 2. Since the A6 fraction of Material III had been found to have an atomic-weight change of approximately one-sixth less than that for the other two samples, it was subjected to an additional diffusion, the light fraction being united with the A6 samples of Materials I and II. This quantity of sodium chloride was then further increased by the addition of Fraction B6, which was produced by successive diffusions on three of the heavier fractions (designated by the letter B) from the first series of diffusions. Those which had resulted from work on Material III were assumed to be uniformly one cut lower in value, and were introduced at their appropriate places, indicated by the asterisks in Fig. 2. The remaining diffusions and combinations of fractions are self-evident from the diagram, and need no further explanation. The amounts of material in the last diffusions were of course, rather small, Fraction A8 consisting of 51 g. of sodium chloride, and C8 of 41. The final material, A9, contained 28 g. of hydrogen chlor-

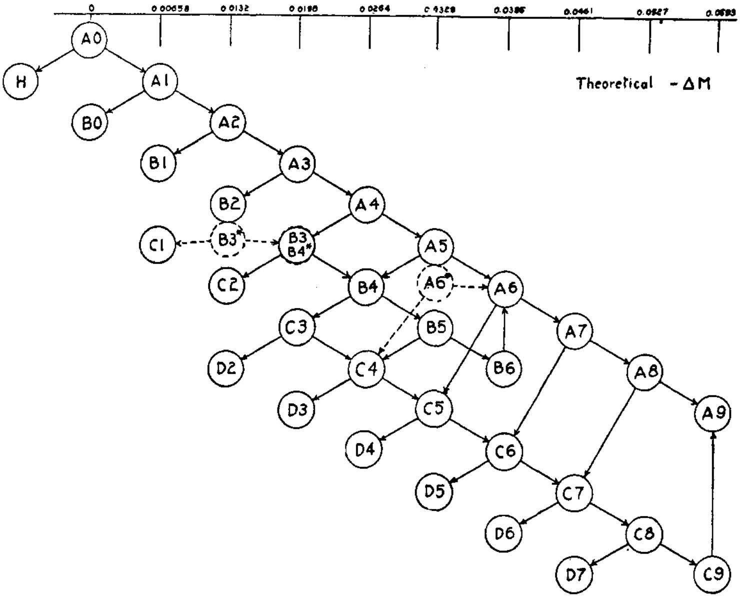


Fig. 2.—Fractionation plan actually used.

ide and, after purification, was subjected to the final series of atomic-weight determinations.

Atomic-Weight Determinations

Purification of Chlorine Compounds.—The hydrogen chloride which was obtained as the light fraction from the sixth diffusion was probably already quite pure. Previous work had shown that the sodium bicarbonate used in this work for neutralizing the fractions does not introduce an appreciable quantity of bromide or iodide. Nevertheless, the acid was subjected to further purification before the analyses were undertaken. The sample used for the first series of experiments on Material II was converted into sodium chloride, dissolved in conductivity water to form a nearly saturated solution, and partially precipitated by the addition of absolute alcohol. The crystals thus obtained were filtered off, dried and treated with chemically pure sulfuric acid. The hydrogen chloride produced was dissolved in pure water, and the acid distilled fractionally. The middle fraction from this distillation constituted the "isotopic" acid for the analysis. All apparatus was made entirely of Pyrex glass. Material III underwent essentially the same treatment, except that the purified salt was obtained by passing isotopic hydrogen chloride into the saturated solution. The very concentrated solution obtained as the mother liquor from this operation gave no test for iodide when treated with nitrous acid and starch solution. This method of detecting iodine in the presence of a large amount of salt has proved to be more sensitive than the nitrosyl-sulfuric acid test. Bromides also were absent when another portion was treated with chlorine water and carbon disulfide.

Other quantities of isotopic material were purified merely by conversion of sodium chloride into the acid, and fractional distillation of the latter. As will be seen in the analyses, material purified in this manner gave the same atomic weight as that which had undergone the more thorough purification process. (Compare the first and second series on Material II.)

The reference acid was ordinary chemically pure hydrochloric acid which had been treated with potassium permanganate crystals, boiled, and fractionally distilled thrice, each time the first and last one-thirds being rejected. This method of purification has been found by Richards[4] to eliminate bromine and iodine completely.

Preliminary Series of Analyses (Fraction A6).—The method used in determining the atomic-weight change for the light fractions from the sixth diffusion consisted of a comparison, by titration, of the concentration of a hydrochloric acid solution of the isotopic material with that of a sample of ordinary pure hydrochloric acid of exactly the same den-

---

[4] Richards, *Carnegie Inst. Publ.*, No. 28, p. 63 (1905).

sity. A complete description of the procedure and calculations involved in these determinations has been given by Harkins and Hayes[2] in connection with their work on the heavy fraction. The analyses reported here were effected in an exactly similar manner, so that it will be sufficient to present the data obtained in two independent series of determinations on each of the three samples which constituted this fraction.

TABLE I

ANALYSES, FRACTION A6

All weights corrected to vacuum standard

PYCNOMETER CONSTANTS

	First series	Second series
Wt. + water (t = 25 ± 0.0005°), g.	35.7399	49.7751
	35.7399	49.7751
Av.	35.7399	49.7751
Wt. of pycnometer, g.	13.9804	18.0824
Volume, cc.	21.8239	31.7867

MATERIAL I

	First series		Second series	
	Reference	Isotopic	Reference	Isotopic
Wt. of pycnometer + acid, g.	37.7698	37.7695	52.8960	52.8959
	37.7700	37.7701	52.8961	52.8960
Av.	37.7699	37.7698	52.8960	52.8959
Difference	0.0001 g. = 0.00074%		0.0001 g. = 0.00064%	
Density	1.09006		1.09525	
Percentage composition	19.06		20.11	
Moles per 1000 g. water	N = 5.23		N = 5.52	
Density of HCl, apparent	1.7868		1.7857	
Volume of 5 g. of acid	4.5870		4.5863	

Data on Titrations—First Day

	First series Reference	First series Isotopic	Second series Reference	Second series Isotopic
N NaOH used, g. per 5 g. of acid	27.4376	27.4912	28.9138	28.9715
	27.4352	27.5018	28.9177	28.9714
Av.	27.4364	27.4965	28.9157	28.9714
Difference (g. of 0.01 N NaOH)	6.01		5.57	

Second Day

	First series Reference	First series Isotopic	Second series Reference	Second series Isotopic
	27.4352	27.4896	28.9137	28.9712
	27.4369	27.4976	28.9191	28.9754
Av.	27.4360	27.4936	28.9164	28.9733
Difference (g. of 0.01 N NaOH)	5.71		5.69	

	Av. difference in titration value	Correction for factor on NaOH	Correction for density difference	Corrected difference
First series	5.86	−0.29	+0.11	5.68
Second series	5.63	−0.27	+0.09	5.43

TABLE I (*Continued*)

Decrease in Atomic Weight

		Calcd.	Found	Efficiency, %
First series		0.0395	0.0382	97
Second series		.0395	.0345	87
	Av.	.0395	.0362	92

23 g. of chlorine obtained of atomic weight 35.421.

MATERIAL II

	First series Reference	First series Isotopic	Second series Reference	Second series Isotopic
Wt. of pycnometer + acid, g.	37.9049	37.9047	56.8995	56.8997
	37.9051	37.9051	56.8997	56.9001
Av.	37.9050	37.9049	56.8996	56.8999
Difference	0.0001 g. = 0.00093%		0.0003 g. = 0.00210%	
Density	1.09626		1.09535	
Percentage composition	20.33		20.12	
Moles per 1000 g. of water	N = 5.57		N = 5.52	
Density of HCl, apparent	1.7856		1.7857	
Volume of 5 g. of acid	4.5612		4.5646	
Data on Titrations—First Day				
N NaOH used, g. per 5 g. of acid	29.2148	29.2612	28.9491	29.0020
	29.2063	29.2686	28.9497	29.0078
Av.	29.2105	29.2649	28.9494	29.0049
Difference (g. of 0.01 N NaOH)	5.44		5.55	
Second Day				
	29.2109	29.2719	28.9512	29.0124
	29.2155	29.2756	28.9554	29.0170
Av.	29.2132	29.2737	28.9533	29.0147
Difference (g. of 0.01 N NaOH)	6.05		6.14	

	Av. difference in titration value	Correction for factor on NaOH	Correction for density difference	Corrected difference
First series	5.74	−0.28	+0.13	5.59
Second series	5.84	−0.28	−0.30	5.26

Decrease in Atomic Weight

		Calcd.	Found	Efficiency, %
First series		0.0395	0.0355	90
Second series		.0395	.0336	85
	Av.	.0395	.0345	87

23 g. of chlorine obtained of atomic weight 35.423.

MATERIAL III

	Reference	Isotopic
Weight of pycnometer + acid	37.5067	37.5071
	37.5075	37.5079
Av.	37.5071	37.5075
Difference	0.0004 g. = 0.00368%	
Density	1.07802	

Percentage composition	16.66
Moles per 1000 g. of water	N = 4.57
Density of HCl, apparent	1.7916
Volume of 5 g. of acid	4.6381

Table I (*Concluded*)

Data on Titrations

	First Day		Second Day	
	Reference	Isotopic	Reference	Isotopic
N NaOH used, g. per 5 g. of acid	23.9665	24.0163	23.9761	24.0256
	23.9725	.....	23.9864	24.0274
Av.	23.9695	24.0163	23.9812	24.0265
Difference (g. of 0.01 N NaOH)	4.68		4.53	

	Av. difference in titration value	Correction for factor on NaOH	Correction for density difference	Corrected difference
First series	4.60	−0.22	−0.53	3.85

Decrease in Atomic Weight

	Calcd.	Found	Efficiency, %
First series	0.0395	0.0294	74

40 g. of chlorine obtained of atomic weight 35.428.

Discussion of Preliminary Results

The possible accuracy in the determination of the density differences of the acids for titration, and in the titrations themselves, was found to be close to that given by the previous investigators. In successive determinations of the density of a given sample of acid, its value increased slightly on account of unavoidable evaporation during the refilling of the pycnometer. However, since both isotopic and reference acids were handled in the same way, it was found that a determination of the difference in densities could be made with sufficient precision to bring the uncertainty in the atomic weight due to this measurement well below that due to the titrations. Computing the average deviation from the mean, in repeated determinations of the same difference in titration value, we find that an error in the atomic weight of 0.001 to 0.002 unit is the maximum which could be introduced by the determination of this quantity.

We may conclude that the probable error in the values for the atomic weights is not greater than 0.002 unit. This is borne out by the fact that the first and second series gave values differing by 0.0037 for Material II, and 0.0019 for Material I, a rather better agreement than was obtained by Harkins and Hayes.

The values given for the theoretical decrease in the atomic weight in this and in later determinations were calculated from the simplified equation of Mulliken and Harkins: $\Delta^{c}M = {}^{-}nB[lnC/(C-1)]$. It will be seen that the efficiencies of the two forms of apparatus are approximately the same, and are higher than those calculated from the results of Harkins and Broeker,[1] and of Harkins and Liggett.[2] These investigators employed the same type of pipestems for the diffusion membrane, but those used in the present work were probably more carefully selected.

Final Atomic Weight Determinations (Fraction A9)

In order to demonstrate conclusively that a separation of the expected magnitude had been effected, a method for determining the absolute atomic weight of chlorine was applied to the ninth diffusate. The procedure was a modification of the second method used by Richards and Wells in their determination of the silver-silver chloride ratio, and involves no transfer of the precipitate.

Silver of the highest purity was prepared by S. B. Stone at the University of Michigan using the method of Richards and Wells. We are indebted to Professors McAlpine and Willard for supervising this purification. About 2 g. of this silver was placed in a long-necked quartz flask, dissolved in nitric acid, and enough aqueous solution of the hydrogen chloride added to convert the silver nitrate completely to silver chloride. After evaporation and drying, the pure white silver chloride was fused, and weighed in the same flask on a balance which gave a 0.5mm. deflection for 0.01 mg. All of the acids were highly purified, and extreme precautions were taken to avoid the loss of material or the gain of impurities. The details of the method are important, but will be omitted here since they will be fully described in a paper by Harkins and Stone on the atomic weight of meteoric and terrestrial chlorine.

Purification of the hydrochloric acid was accomplished by methods already described, the simpler one being used in the case of the isotopic acid. No change in atomic weight for the latter was observed when it was subjected to a further distillation. This is regarded as the best evidence for the absence of impurities likely to render the atomic weight too low.

Results of Final Series of Atomic Weight Determinations.—In order to show the magnitude of the corrections involved, the results of a typical experiment with the isotopic material are given in Table II.

TABLE II

EXPERIMENT O

Corr. wt. of Ag in air, g.	1.32082
Vac. corr., g.	−0.00004
Wt. of Ag in a vac., g.	1.32078
Excess wt. of flask over counterpoise, g.	1.59978
Excess wt. of flask and fused AgCl over counterpoise, g.	3.35405
Wt. of AgCl in air, g.	1.75427
Vac. corr. for AgCl and extra wts.	0.00013
Change in d. of air	−0.000039
Change in vac. corr. for excess vol. of flask over counterpoise	0.00002
Vac. corr.	0.00015
Wt. of AgCl in a vac.	1.75442
Residue corr.	−0.00005
Corr. wt. of AgCl	1.75437

AgCl:Ag = 1.75437:1.32078 = 1.32828

Cl = 35.415

Four experiments with chlorine from ordinary, purified hydrochloric acid gave an average result in exact agreement with the accepted value.

ANALYSES; ORDINARY CHLORINE

Expt.	Obs. wt. of Ag (vac.)	Obs. wt. AgCl (vac.)	Parts of AgCl per 100 parts of Ag	At. wt. of Cl (Ag = 107.880)
k	1.78992	2.37824	132.868	35.458
l	2.09738	2.78678	132.869	35.459
m	1.66813	2.21636	132.865	35.455
n	1.86118	2.47288	132.866	35.456
			Av. 132.867	35.457

Silver prepared in the same lot as that used for the above series served in making the analyses of the final, purified isotopic material.

ANALYSES; FRACTION A9

Expt.	Obs. wt. of Ag (vac.)	Obs. wt. of AgCl (vac.)	Parts of AgCl per 100 parts of Ag	At. wt. of Cl (Ag = 107.880)
o	1.32078	1.75437	132.828	35.415
p	1.16019	1.54108	132.830	35.417
		After another distillation		
q	1.42781	1.89659	132.832	35.419
r	1.43282	1.90321	132.830	35.417
s	1.05716	1.40424	132.832	35.419
t	1.75764	2.33470	132.832	35.419
			Av. 132.831	35.418

Discussion of Results for Final Series.—Twenty-eight and one-tenth g. of chlorine has been obtained of atomic weight 35.418, a decrease of 0.039 unit. The calculated change in atomic weight for the ninth diffusate is —0.0593 unit. The efficiency of the entire series of diffusions is, therefore, 66%. Considered in connection with the results of the analyses of Fraction A6, this indicated that the efficiency of the last three diffusions was surprisingly low. Three factors may have entered in bringing this about; of these the second is undoubtedly responsible for almost all of the lowering of efficiency: (1) an accidental mixture of fractions of unlike value; (2) *the difficulty of realizing efficient diffusions with small amounts of material* and a large apparatus and failure to free the apparatus completely from one sample of the gas before the next is introduced; (3) failure to obtain a cut of exactly 2.

Summary

1. Chlorine of atomic weight 35.418, or 0.039 unit lower than for ordinary chlorine, has been produced by a systematic series of cuts of 2 in diffusions through the walls of porous porcelain pipestems. This increases the separation produced in this Laboratory to 0.097 or approximately one-tenth of a unit of atomic weight, or to a difference of 1 part

in 365, by far the greatest relative difference produced in the atomic weight of an element. The atomic weights were obtained by determining in quartz flasks the ratio of the weights of highly purified silver to extremely pure silver chloride. The method involved no transfer of silver or silver chloride from one vessel to another, since in each determination all of the significant operations and all of the weighings were carried out with one quartz flask.

2. The above results refer to the ninth cut of 2. In order to compare the relative efficiencies of the different sets of apparatus used, three determinations were made by the density method of Harkins and Hayes after the sixth cut of 2. These showed atomic-weight lowerings of 0.036, 0.034 and 0.029 for the three independently obtained samples.

CHICAGO, ILLINOIS

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

INTERFACIAL TENSION AND EMULSIFICATION. I. THE EFFECTS OF BASES, SALTS, AND ACIDS UPON THE INTERFACIAL TENSION BETWEEN AQUEOUS SODIUM OLEATE SOLUTIONS AND BENZENE. II. EXTREMELY SMALL INTERFACIAL TENSIONS PRODUCED BY SOLUTES[1]

BY WILLIAM D. HARKINS AND HENRIETTA ZOLLMAN

RECEIVED AUGUST 17, 1925 PUBLISHED JANUARY 8, 1926

Introduction

It has long been recognized that stable emulsions of oils in water form readily if solutes which greatly lower the interfacial tension are present.[2] According to Gibbs[3] such solutes are highly adsorbed at the interface, and the importance of the films thus formed in stabilizing emulsions has been pointed out by Bancroft.[4] It is obvious that the interfacial tension and the extent to which interfacial films are formed are not entirely independent variables, so a comprehensive theory of emulsions should take account of these two factors. The interfacial tension is affected by the electrical charges at the interface, and these electrical charges undoubtedly play an important role in emulsification.

Attainment of Equilibrium

Measurements were made of the interfacial tension at the phase boundary between benzene and aqueous solutions of sodium oleate alone or plus

---

[1] An abstract of this paper was presented to the Second Annual Colloid Symposium, June, 1924. "Colloid Symposium Monograph," **2,** 172 (paragraph 9).

[2] Quincke, *Pogg. Ann.*, **139,** 1 (1870); *Wied. Ann.*, **35,** 571 (1888).

[3] Gibbs, "Scientific Papers," Longmans & Co., Vol. 1, **1906.**

[4] Bancroft, *J. Phys. Chem.*, **17,** 514 (1913); **19,** 275 (1915).