

the concentrated solutions has been explained by assuming a considerable increase in the viscosity of the solution as the concentration increased with a corresponding decrease in the mobility of the ions.

(4) The decrease in the molecular conductivity with dilution over the greater part of the curve plotted in Fig. 1 is explained by assuming a complex electrolyte, containing  $n$  molecules of solute. The expression for the molecular conductivity is then  $kv^n$  rather than  $kv$ .

(5) The best conducting solution for the above solutes has a specific conductivity of 0.007 reciprocal ohms.

(6) The temperature coefficients for ethyl and butyl alcohols are very large and increase with the concentration. This is explained by assuming a large decrease in the viscosity of the solution with the temperature, this decrease being greater the more concentrated the solution. In the case of resorcinol the effect of the decrease in viscosity with temperature is great enough to change a negative temperature coefficient for a dilute solution, to a positive coefficient for a concentrated solution.

(7) The molecular conductivities of the above alcohols and of acetic acid in liquid hydrogen bromide and chloride are compared, the hydrogen chloride solutions being much the better conductors.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

## THE ATOMIC WEIGHT OF FLUORINE.

[PRELIMINARY PAPER.]

BY D. J. MCADAM, JR., AND EDGAR F. SMITH.

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The present communication brings an account of experiments made to determine the atomic weight of fluorine by a new method. As the work has to be interrupted for a time it was concluded to offer such results as have been obtained.

A record of all previous work on the atomic weight of this element may be found in the third edition of F. W. Clarke's "A Recalculation of the Atomic Weights." Most determinations have been made by changing various fluorides into sulfates. This was the method pursued by Berzelius, Louget, Dumas, De Luca and Moissan, who used the fluorides of calcium, barium, lead, sodium and potassium. Their results vary from 18.85 to 19.14. The chief sources of error in the method are incomplete change of fluoride into sulfate, and loss of material due to the violent escape of hydrofluoric acid. Louget writes that, in spite of all precautions, there was always a slight loss of material. Naturally both these sources of error would lead to high values for the atomic weight.

Christensen<sup>1</sup> treated ammonium manganese fluoride,  $(\text{NH}_4)_2\text{MnF}_6$ ,

<sup>1</sup> *J. prakt. Chem.*, [2] 35, 541.

with potassium iodide and hydrochloric acid, and titrated the liberated iodine. In this way he obtained four values for the ratio  $(\text{NH}_4)_2\text{MnF}_5 : \text{I}$ , the extreme variation being a little over 0.1% and the atomic weight 19.038. As Julius Mayer<sup>1</sup> has pointed out the iodometric method is subject to error, since some iodine is set free by the action of the hydrochloric acid on the potassium iodide. Moreover, Christensen gives no proof that his ammonium manganese fluoride did not contain other double fluorides of manganese.

Julius Mayer made five determinations of the ratio  $\text{CaO} : \text{CaF}_2$ . He prepared calcium oxide with great attention to removal of impurities and ignited to constant weight. He was unsuccessful in attempting to change calcium oxide to calcium fluoride by the direct treatment of the hydrated lime with hydrofluoric acid, as the material always gave an alkaline reaction when moistened. So he first treated the lime with hydrochloric acid, and then evaporated the chloride repeatedly with hydrofluoric acid to convert it into the fluoride. Special precautions were taken in ignition of the fluoride to constant weight. He has given no proof, however, of the completeness of the reaction, except to mention that the substance was neutral to litmus.

In this laboratory, we sought to change sodium chloride to fluoride by evaporation with hydrofluoric acid and, after seven evaporations, found much chloride remaining. Unless Mayer's term "mehrere" means much more than seven evaporations with hydrofluoric acid it is probable that his calcium fluoride contained traces of chloride, which would make his value for the atomic weight of fluorine, 19.035, somewhat too high.

It seemed desirable to try some other method. It was determined to change sodium fluoride into chloride with dry hydrochloric acid gas. It was hoped by this means to avoid the loss of material.

#### Preparation of Pure Material.

*Water.*—Ordinary distilled water was redistilled with addition of a little permanganate and alkali, a glass condenser being used. To the distillate a few drops of sulfuric acid were added and it was again distilled, using a quartz condenser. In most cases it was further redistilled from a Jena flask, employing a platinum condenser. It was either collected directly in platinum, or in flasks of Jena resistance glass, with covers ground on to the outside. No corks or rubber connections were used, and special care was taken to exclude dust.

*Sodium Fluoride.*—This was prepared from the acid fluoride,  $\text{NaHF}_2$ , by heating the latter in a current of dry nitrogen or air. Since sodium fluoride is alkaline in reaction, it is evidently hydrolyzed by moisture; if heated in ordinary air, it is probable that some of the fluorine is replaced by hydroxyl.

<sup>1</sup> *Z. anorg. Chem.*, **36**, 313 (1903).

The apparatus used in preparing the nitrogen consisted of a long, electrically heated Jena tube containing spirals of copper gauze. Through this tube, air saturated with ammonia was passed. It was then conducted through two U tubes containing dilute sulfuric acid to remove excess of ammonia, through a tower containing glass beads moistened with silver nitrate solution, through a bottle and tower containing concentrated sulfuric acid, through a tower containing small pieces of potassium hydroxide, through two towers containing boiled sulfuric acid, and finally through a long tube containing phosphorus pentoxide. The latter had been resublimed in a current of dry air directly into the tube in which it was to be used. All the apparatus, forward from the tube containing the copper gauze, was constructed of glass with ground joints. When a current of dry air was desired, ordinary air was forced through the same apparatus, after removal of the tube containing the gauze.

*Sodium Hydrogen Fluoride (Sample A).*—Very pure sodium carbonate was dissolved in pure water, the solution filtered and crystallization allowed to occur in platinum. The product was washed once by decantation and three times by centrifugal drainage. The centrifugal machine held two perforated platinum cones, and the average speed was 1500 revolutions per minute. The sodium carbonate was then considered to be pure enough for use in preparing acid sodium fluoride.

Commercial hydrofluoric acid was treated with one-fourth its equivalent of potassium fluoride, in order to form potassium silicofluoride from the silica present. A little potassium permanganate was also added in order to decompose any chloride that might be present. It was next distilled from a lead retort, with lead condenser, the retort being placed in a paraffin bath at  $120^{\circ}$ , since potassium silicofluoride is not decomposed at that temperature. The first fourth of the distillate, containing most of the chlorine, was rejected. It was then redistilled with addition of a little potassium fluoride and permanganate, rejecting the first portion as before. After four distillations, the last half of the distillate was found to be free from chlorine. It was then distilled three times from a platinum retort, rejecting the first and last portion each time. Traces of lead were thus completely removed.

From the last distillation, the liquid was collected in a platinum flask and was added to a portion of the sodium carbonate solution prepared as described above and contained in platinum dishes. At first the sparingly soluble sodium fluoride appeared, and being semi-gelatinous, it could not be centrifuged, but was allowed to settle and the supernatant liquid was decanted. To this sodium fluoride enough more hydrofluoric acid was added to produce the acid fluoride,  $\text{NaHF}_2$ . This consists of small crystals, considerably more soluble in hot than in cold water, which can be centrifuged without difficulty. To test the purifying effect of this

scheme of crystallization, a portion of the crystals was mixed with sodium chloride and treated with silver nitrate, when a heavy precipitate appeared. But, after one recrystallization, only a slight precipitate occurred, while after two crystallizations, no test for chlorides was obtained.

The acid fluoride, after being centrifuged, was preserved in platinum dishes over solid potassium hydroxide, in desiccators thickly lined with paraffin. Every few days, the salt was stirred and all lumps were broken by gentle rubbing with a platinum spatula.

*Sodium Hydrogen Fluoride (Sample B).*—A portion of sample A was recrystallized from water containing a little hydrofluoric acid, centrifuged and preserved as in A.

*Sodium Hydrogen Fluoride (Sample C).*—A portion of sample B was again recrystallized and treated as before.

*Balance and Weights.*—The Troemner balance used in previous atomic weight work in this laboratory was again employed. Successive weighings of the same object agreed within 0.02 or 0.03 milligram.

The large weights were of brass, gold-plated, and the small weights were of platinum. They were of Class B, Bureau of Standards, and were carefully standardized.

The apparatus for carrying out the reaction is shown in Fig. 1; it was constructed entirely of platinum. A is a large tube drawn

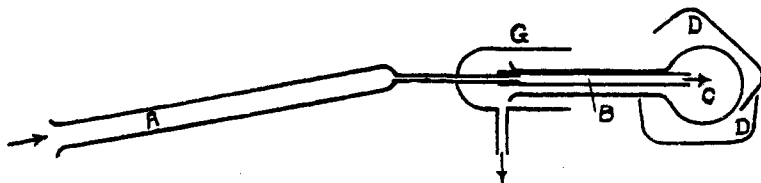


Fig. 1.

out to form a small tube at one end. B is the inner tube belonging to the flask C; it could be slipped over the small end of the tube A, and formed a support strong enough to hold the flask C. So the flask C, which was to contain the sodium fluoride, was supported entirely from the inside, and could be rotated so as to cause the sodium fluoride to roll around and expose fresh surface. D, D are platinum dishes, the upper being placed inside the lower and thus supported so as not to touch the flask C. These dishes were heated by Bunsen burners above and below, and the temperature of the air in this platinum oven could be regulated within ten degrees. G is a platinum tube, with small side tube through which the fumes were drawn by suction into an absorption apparatus. Fig. 2 shows the flask, with inner tube and stopper, in position for weighing. The stopper E fits it tightly enough to prevent diffusion, but not enough to make it air-tight.

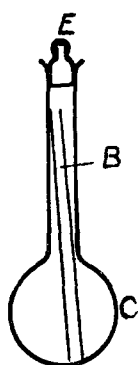


Fig. 2.

To the large end of the tube A, the tube from the nitrogen apparatus, or the tube from the hydrochloric acid generator, as the case might be, was adjusted by a ground glass joint.

The hydrochloric acid generator was constructed entirely of glass, with connections of ground glass or sealed by sulfuric acid. The gas was obtained by allowing sulfuric acid to drop into hydrochloric acid solution. It passed through a bottle of strong hydrochloric acid, and a bottle and tower containing sulfuric acid, and thence into tube A of the platinum apparatus. Enough acid was used in the apparatus to run an experiment continually for about forty hours.

#### Analytical Process.

The platinum flask, with inner tube and stopper in place, was weighed. Since sodium fluoride is slightly hygroscopic, it was necessary to weigh the flask filled with dry air. All weighings were by substitution of a counterpoise having nearly the same weight and surface as the flask. Platinum-tipped tongs were used in handling the flask. The acid sodium fluoride was now placed in the weighed flask and the apparatus was arranged as in the diagram.

After heating in a current of nitrogen, the flask and inner tube were removed and stoppered quickly to exclude moist air, and placed near the balance for several hours before weighing.

The experiments may now be described in the order in which they were performed.

*Experiment (1).*—Some sodium hydrogen fluoride (Sample A) was heated in the weighed flask for a period of four hours in a current of dry nitrogen at  $325^{\circ}$ , the nitrogen replaced by dry air and the flask restoppered and weighed.

Weight of NaF = 4.3281 grams; heated to  $450-510^{\circ}$  for four hours. Weight of NaF = 4.3278 grams, and in dry air at  $500^{\circ}$  for two hours. Weight of NaF = 4.3274 grams.

It was thought that possibly the slight decrease in weight was due to hydrolysis, but later experiments with the vacuum desiccator showed the lower weight to be more nearly correct. So the weight of the sodium fluoride was taken as 4.3274 grams.

Dry hydrochloric acid gas was then passed over it, with frequent turning of the flask, the acid being finally displaced by dry air at about  $400^{\circ}$ . The duration of treatment with hydrochloric acid, with temperatures and weighings are given below and show the progress of the reaction. Its curve is similar to that of a reaction of the first order.

Time. Hours.	Temperature.	Weight. Grams.
8	370°	5.7749
9 <sup>1</sup> / <sub>2</sub>	400°	5.9899
10 <sup>1</sup> / <sub>2</sub>	440°	6.0019
10	460°	6.0088
10	460°	6.0131
11	470°	6.0167
10	450°	6.0176
10	460°	6.0186
34	460°	6.0204
35	460°	6.0213
24	460°	6.0211

The outside of the flask was rinsed with hydrochloric acid and then reheated in a current of dry air at 440° for an hour.

Weight of NaCl = 6.0209 grams.

The salt was again exposed to hydrochloric acid gas for 7 hours at 520°.

Weight of NaCl = 6.0208 grams.

With stopper loosely in place, the flask was held inclined in the blast flame until the contents could be seen, through the hot translucent platinum, to be entirely liquid:

Weight of NaCl = 6.02075 grams.

Constant weight was reached after heating through 180 hours. It was hoped that the reaction was complete; conditions seemed favorable, since the sodium fluoride was in a porous condition after the escape of hydrofluoric acid from the acid fluoride.

Assuming 58.46 as the molecular weight of sodium chloride, the molecular weight of sodium fluoride calculated from this experiment would be  $58.46 \times \frac{4.3274}{6.0208} = 42.0176$ . If sodium is 23.000, the atomic weight of fluorine would be 19.0176.

Since no very delicate test for fluorides in the presence of chlorides had been worked out, the material was saved with the purpose of investigating it later.

*Experiment (2).*—This was a special experiment to learn how constant and definite a weight of sodium fluoride could be obtained by heating the acid fluoride in dry nitrogen or air.

4.85 grams of NaHF<sub>2</sub> (Sample C) were treated in the weighed platinum flask with dry nitrogen, in the cold, for an hour to remove traces of moisture, then for eight hours with a gradual rise of temperature from 350° to 520°. The nitrogen was then displaced by dry air.

Weight of NaF = 3.26104 grams.

It was then reheated in dry air at 450° to 500° for 4<sup>1</sup>/<sub>2</sub> hours, stoppered quickly and placed in a vacuum desiccator. The air was quickly removed from the desiccator (and flask) and allowed to reenter after passing suc-

cessively through a tower containing pieces of potassium hydroxide and a tower containing glass beads moistened with boiled sulphuric acid. This process was used in all later weighings of the flask:

Weight of NaF = 3.26098 grams.

With the stopper of the flask loosely in place, the sodium fluoride was next fused in the blast flame; the material was seen to melt to a mobil liquid, its melting point being about  $900^{\circ}$ . While still hot it was transferred to the vacuum desiccator and treated as before.

Weight of NaF = 3.26098 grams.

It was fused again, cooled to dull redness, re-fused, and treated in the vacuum desiccator as before.

Weight of NaF = 3.26088 grams.

So the extreme variation of these four weighings is 0.00016, after two fusions. Some of the loss may be due to the sodium fluoride or even to the platinum itself.

This and the preceding experiment, therefore, prove that sodium fluoride may be brought to definit weight by the method of heating in a current of dry nitrogen or air, and that the weight is constant over a range of nearly  $600^{\circ}$ .

It also proves that the fluoride, when thus treated, contains no weighable amount of absorbed air.

*Experiment (3).*—Sodium hydrogen fluoride (Sample C) was treated with dry nitrogen in the cold for an hour, then with gradual rise of temperature from  $300^{\circ}$  to  $500^{\circ}$  for six hours with frequent turning. It was then treated in the vacuum desiccator as in previous experiments.

Weight of NaF = 3.3940 grams.

The salt was reheated in dry air at  $500^{\circ}$  for four hours:

Weight of NaF = 3.39398 grams.

The last weight was taken as correct, and the salt was heated in hydrochloric acid gas as in Experiment (1).

Time. Hours.	Temperature.	Weight. Grams.
56	$450^{\circ}$	4.7211
29	$450^{\circ}$	4.72194
39	$450^{\circ}$	4.72232
35	$450^{\circ}$	4.72244
41	$450^{\circ}$	4.72292

—  
Total 200

We abandoned the idea of obtaining constant weight by this method. Evidently some fluoride in the interior of each granule is not easily reached.

With stopper loose, the sodium chloride was now fused:

Weight of NaCl = 4.72260 grams.

It was thought that possibly the continued, small increase in weight was

due to minute particles of platinum being rubbed off from the entrance tube and falling into the flask; but, after rinsing, no increase in the weight of platinum was found, so the increase in weight must have been due to the chemical reaction alone.

The molecular weight of sodium fluoride calculated from this experiment would be  $58.46 \times \frac{3.39398}{4.72260} = 42.0133$ , and the atomic weight of fluorine would be 19.0133.

In future work we shall modify the scheme to ensure absolute removal of fluorine, the detection of which in small amount is at present very uncertain and extremely difficult. The treatment with dry hydrochloric acid gas will be followed by moistening with water and evaporating so as to expose fresh surface.

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## A NEW METHOD FOR THE QUANTITATIVE ANALYSIS OF SOLUTIONS BY PRECISE THERMOMETRY.

[PRELIMINARY PAPER.]

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This paper describes concisely a new method of analyzing solutions which may be of very general application both in technical and in scientific work. The method depends upon noting the precise temperature at which the unknown solution attains exactly the same density as a given, previously calibrated solid float. This equality in density is marked by the familiar phenomenon, which we may call "floating equilibrium," where the wholly immersed solid neither rises nor sinks in the liquid. When, as is usual, the solution is denser than the solvent, the more concentrated the solution, the higher is the temperature necessary to reach floating equilibrium; hence, each concentration corresponds to a definite temperature, and after a few points on the almost linear curve connecting the two variables have been determined by means of known solutions, all the intervening ones are determinable by simply reading the thermometer at the points where floating equilibrium is attained. When the solution is less dense than the solvent, precisely the same method is used, except that the solution must be cooled instead of warmed to attain floating equilibrium, as the concentration increases. One should note that *differences* alone are the subject of study by this method; the exact density of none of the solutions need be known. The method is indeed more sensitive and accurate than any of the usual methods of determining the densities of liquids. The starting-point in each case should be the perfectly pure solvent, whose density, again, need not be