

potential readings astray. Experiments have shown, however, that no measurable error is recorded even after the contact key has been closed for a full minute, unless the potentiometer is set much more than 20 millivolts off the null point. Even when the setting was as much as 100 millivolts off the null point the potential returned to normal within a few seconds of rest. Such abuse should not occur in practice; in fact, it would actually send the galvanometer marker entirely off the scale, twist the suspension, and require a new zero setting. It is likely that the increase in conductivity provided in these electrodes has brought an increase in resistance to polarization with a given current flow.

It was noted, however, that in cases where the electrode was polarized with large currents it did not return to normal potential as rapidly as would a quinhydrone electrode. Obviously one should avoid long periods of key contact.

Silver-Silver Chloride Electrodes

Some workers may prefer to use the silver chloride electrode in place of the calomel electrodes here described. In this way one might eliminate the potassium chloride-agar bridge

which, though simple and easy to prepare, is not permanent. The silver electrode would be placed directly in the glass electrode bulb. Details of the silver electrodes have been given by MacInnes and Beattie (3) and MacInnes and Dole (4).

Acknowledgment

The writer wishes to thank James B. Conant, and also the Corning Glass Company, for suggestions and materials in connection with this work.

Note—Since the writing of the foregoing account, an abstract [C. A., 24, 4188 (1930)] has been published giving a report of the work of C. Morton with glass electrodes of character similar to those described above, but with different electrical accessories and technic.

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Methods for Determining the Solubilities of Some Fluosilicates¹

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THE fluosilicates have recently attracted considerable attention due to their use as insecticides and fungicides, in waterproofing and hardening concrete, in electroplating, etc. However, quantitative data in connection with these substances are not numerous and usually of questionable accuracy. Carter (2) has recently published the solubility curves for barium, potassium, and sodium fluosilicates, together with a compilation of all available solubility figures on the fluosilicates. Methods of analysis, likewise, are not all that might be desired.

This paper presents the solubilities and densities, both at 20° C., of the fluosilicates of sodium, magnesium, zinc, lead, and copper. It includes also a brief discussion of the analytical methods.

Apparatus

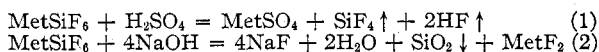
The apparatus deemed most suitable for the purpose was that of Bahr (1). The air used for stirring was first passed through a mercury pressure regulator, by which the rate of flow was maintained constant at 4 bubbles per second. Thence it passed in succession through three Drechsel gas-washing bottles (equipped with petticoat bubblers) containing sodium hydroxide solution, water, and the solution being saturated. Tests showed that the air current produced no decomposition of the fluosilicates above that taking place when the air stream was stationary. Saturator and pycnometer were arranged exactly as described by Bahr, save that a single three-way cock was used in place of two ordinary cocks. A small test tube equipped with an air vent was attached to the pycnometer so as to catch the overflow produced during filling. The whole apparatus was connected by means of ground-glass

joints covered with rubber tubing and was completely immersed in an automatic thermostat adjusted to $\pm 0.5^\circ$ C. No leakage through the submerged joints was observed at any time. A small filter of packed asbestos fiber was formed in a conical tube inserted between saturator and pycnometer. The solutions, after passing the filter, were always absolutely clear. A Sprengel pycnometer of about 6.8 cc. capacity was used. All weights and volumetric apparatus were carefully calibrated. Nearly saturated solutions were made in a flask before placing in the saturator. At least 2 hours were allowed to elapse before the first sample was removed from the saturator. Successive samples never showed any trend in analysis.

Analytical Methods

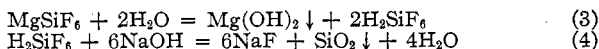
The fluosilicates have the general formula $\text{Met}(\text{SiF}_6)$. The water of crystallization varies from 0 to 6 molecules. They are efflorescent and also decompose slowly, especially those of the heavy metals.

They are all decomposed rapidly by hot sulfuric acid and by hot sodium hydroxide as follows:



The first reaction is quantitative and the second may or may not be, depending on the extent of hydrolysis, etc.

Hydrolysis is very slight in the case of the alkali fluosilicates, but more marked with the others—e. g., MgSiF_6 .

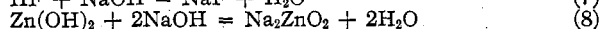
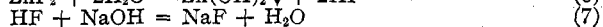
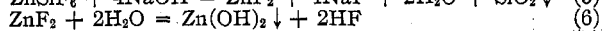
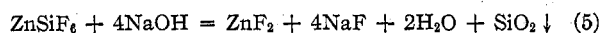


Since the methods of analysis used are based on Reactions 1 and 2, it is obvious that hydrolysis will occasion an error in the results when Reaction 2 is used. Reaction 2 requires 4 mols of alkali per mol of fluosilicate whereas Reaction 4 requires 6 mols. Hence volumetric methods of estimation

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for fluosilicates that hydrolyze must be viewed with suspicion. The degree of hydrolysis varying with temperature and concentration, it is obvious that variable results are likely to be observed. This accords exactly with the writers' experience.

When the fluosilicates of amphoteric substances are studied, volumetric methods become still more dubious. Consider ZnSiF_6 :

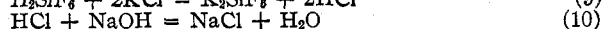
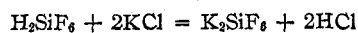


The extent to which Reactions 6 and 8 proceed depends on temperature, concentration, and H-ion concentration.

For these reasons the first method of analysis was used with zinc, lead, and copper fluosilicates. The sample of fluosilicate was heated to vigorous fuming with sulfuric acid containing a little nitric acid. No trace of silica was observed after this treatment. When cool, the trace of iron usually present was precipitated with ammonium hydroxide and filtered off, thus leaving a pure metal sulfate solution for appropriate analysis.

Owing to hydrolysis, free acid figures on the salts are not particularly valuable except to show the magnitude.

The method used by the writers, that of Jacobson (4), consists in adding ice and an excess of potassium chloride, then titrating with sodium hydroxide.



Phenolphthalein was used as indicator with sodium and magnesium fluosilicate and methyl red with zinc fluosilicate.

Preparation and Analysis of Salts and Data

HYDROFLUOSILICIC ACID—This was a very pure and concentrated acid obtained as condensate from the gas tunnel from the hot dens of a phosphate rock acidulating plant.

SODIUM FLUOSILICATE—This salt was prepared in two ways:

(1) Nearly the theoretical amount of the purest sodium chloride was added to a solution of fluosilicic acid containing 100 grams of the acid per liter. Precipitation was immediate. To prevent the formation of a gel, the mother liquor was filtered off immediately and the crystals were washed with cold water on the filter. They were then dried at room temperature.

(2) The procedure was the same as under (1) save that acid sodium carbonate was added slowly.

The crystals made by the first method analyzed 100.05 per cent Na_2SiF_6 , those by the second method, 99.41 per cent. Crystals made by the first method were used in the solubility determinations. They were fine, white, and opaque. No free acid was found. The solution was titrated hot with sodium hydroxide, using phenolphthalein as indicator. Carter (2) found 0.690 per cent (by interpolation from his table).

The results on this and the other salts will be found in Table I. Each value represents the mean of from four to thirteen determinations.

Table I—Solubilities of Some Fluosilicates at 20° C.

SALT	SPECIFIC GRAVITY 20°/4° C.	SOLUBILITY %	AV. DEVIATION FROM MEAN %
Na_2SiF_6	1.0054	0.733	±0.002
$\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$	1.2395	37.94	±0.29
$\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$	1.4336	49.94	±0.23
$\text{PbSiF}_6 \cdot 4\text{H}_2\text{O}$	2.4314	81.90	±0.1
$\text{CuSiF}_6 \cdot 4\text{H}_2\text{O}$	1.6174	59.08	±0.11

MAGNESIUM FLUOSILICATE—A very pure commercial product was used as the source of this salt. Recrystallization

did not improve the purity. The salt was made by dissolving magnesite in a slight excess of dilute fluosilicic acid, evaporating at 77° C. with agitation, allowing the silica to settle out, and crystallizing at 41° C. under reduced pressure. The crystals were dried in a rotary drier. The salt analyzed 101.53 per cent $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$. The free acid was found to be 0.83 per cent. Magnesium fluosilicate forms large, water-clear crystals. Its saturated solution is slightly viscous. Although hydrolysis is not excessive, the fluosilicic acid and magnesium hydroxide are quite gelatinous and make filtration difficult.

The solutions were analyzed volumetrically in the same way as the sodium fluosilicate solutions. As a check magnesium was determined gravimetrically as the pyrophosphate according to the method described by Scott (5).

The volumetric results are so much more concordant that it seems safe to accept them as final. The tediousness of the gravimetric method is probably responsible for the differences observed. Only the volumetric results are given.

ZINC FLUOSILICATE—The zinc fluosilicate likewise was a very pure commercial product. It was made in the same manner as the magnesium fluosilicate, except that zinc oxide was used instead of magnesite. The analysis was 95.58 per cent $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$. The crystals contained 0.79 per cent free acid. The crystals in appearance resemble those of the magnesium salt. The saturated solution is quite viscous. However, filtration is relatively easy, since the hydrolysis products are not very gelatinous.

For reasons already advanced, the volumetric method of analysis is not feasible with this salt. The zinc was therefore precipitated as ZnNH_4PO_4 in neutral solution and ignited and weighed as the pyrophosphate. The method of Fales and Ware (3) was used on several samples and found to give results identical with the pyrophosphate method. The data given are based on the latter method.

LEAD FLUOSILICATE—This salt was prepared by adding about 10 per cent less than the theoretical amount of red lead to a dilute fluosilicic acid solution. Strong acid produces too much decomposition of the salt because of the excessive rise in temperature. Silica and lead dioxide are formed in the reaction and must be filtered off. The solution so formed was allowed to crystallize at room temperature. The crystals analyzed 99.96 per cent $\text{PbSiF}_6 \cdot 4\text{H}_2\text{O}$. This high purity was probably due to the insolubility of lead fluoride.

Lead fluosilicate is the most unstable of all those studied. Slow thermal decomposition proceeds even at room temperature. In consequence the dry salt and its solutions are very corrosive. The crystals are large, clear, and highly refractive. If allowed to stand exposed to the air, they become opaque. The saturated solution is very viscous and hydrolyzes slowly on standing, with the formation of an opaque, white precipitate.

Volumetric methods cannot be used in the analysis of these solutions, so the lead was precipitated as the chromate according to Scott (5). When the saturated solution was diluted, a precipitate formed which was cleared up with nitric acid.

COPPER FLUOSILICATE—This salt was prepared in four different ways:

(1) 10 per cent fluosilicic acid solution plus about 10 per cent less than theoretical C. P. cupric oxide.

(2) Same as (1) but using C. P. basic copper carbonate.

(3) and (4) Same as (1) and (2) but using 30 per cent acid.

Recrystallization of the product formed by each one of the four methods gave crystals identical in all their properties. Crystallization and drying were carried out at room temperature. The crystals are a clear, sparkling blue and are quite

efflorescent. They must be preserved in a carefully stoppered bottle. The saturated solution is viscous. The crystals used analyzed 99.95 per cent $\text{CuSiF}_6 \cdot 4\text{H}_2\text{O}$. Copper was determined iodometrically according to Scott (5).

Acknowledgment

Thanks are due to G. C. Connolly for advice and supervision during the progress of this work and to the Davison

Chemical Company for the use of their analytical laboratory.

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- (5) Scott, *Standard Methods of Chemical Analysis* (1925).

Device for Estimation of Density of Gems and Small Amounts of Solids¹

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IT IS frequently eminently desirable to determine rapidly the density or specific gravity of small amounts of solids too minute to be determined by the more usual methods available to the investigator. The device to be described is particularly adapted for the determination of the density of extremely small quantities of substances, cut gems, and small mineral crystals or fragments.

There are several methods available for the determination of the density or specific gravity of solids (4). These involve the use of: (1) the chemical balance, (2) the pycnometer, (3) heavy liquids and the Westphal balance, and (4) the Jolly balance.

These methods, with the possible exception of the third, are not adaptable to small amounts of solids. The use of heavy liquids is time consuming and the limit of accuracy seems to be 0.03 (5). Furthermore many substances are encountered with a higher density than the heaviest liquid obtainable. The use of a wax and red lead float or the use of clips with small specimens is not compatible with accuracy (7). Caley (1) has perfected an ingenious instrument for the determination of densities that is both accurate and rapid, but not adaptable for substances lighter than the displacing liquid nor specimens it is not desirable to crush, as in the case of gems.

The principle of this device is relatively simple. A narrow tube is filled with a suitable liquid to a mark on a side capillary tube. The sample is inserted in the liquid, and more liquid added from a weight buret to bring the liquid level with a second mark on the capillary tube. The weight of liquid required to fill the instrument from the lower mark to the higher one is previously determined. By subtracting the weight of liquid required to bring the volume from the first to the second mark when the sample is in the tube, from the weight required when the instrument is empty, gives the weight of liquid displaced by the specimen. Since the density of the liquid is known the volume of the specimen can be obtained by a simple calculation, and this value divided into the weight of the specimen gives the desired density.

The method is simple, relatively rapid, and quite accurate.

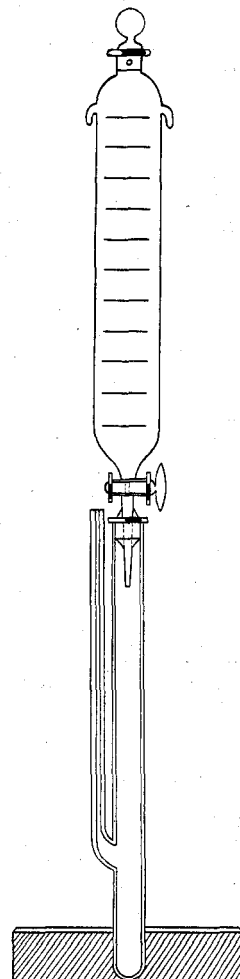
Description of Instrument

The device is constructed of glass and is 12.0 cm. in height with an internal diameter of 0.6 to 0.8 cm. The base may be a glass or wooden block with a single hole large enough to hold the inserted tube upright. The capillary tube has an internal diameter of 1.0 mm. and should widen gradually

to the point of attachment to the main body of the instrument to prevent the inclusion of air bubbles when the instrument is being filled with liquid. It is important that the internal diameter of the capillary shall not exceed 2.0 mm. or be smaller than 1.0 mm. A larger diameter means loss of accuracy when the specimen is very small while a smaller diameter leads to difficulties due to the inclusion of air bubbles when filling the instrument. The capillary should rise to a considerable height, 3.0 to 4.0 cm., above the highest liquid level in order that loss of liquid by evaporation and consequent loss in accuracy may be reduced to a minimum. It has been found by experiment that loss due to evaporation in the capillary under these conditions is negligible over short periods of time. A small weight buret was designed for the instrument bearing in mind several advantages mentioned by Friedman and LaMer (3). However, any weight buret of small size is adaptable to this instrument. It is essential that the buret be fitted with a glass cap and the ground surface for the cap should securely fit the top of the instrument to prevent any loss by evaporation when using very volatile liquids for displacement.

Displacement Liquids

Water may be used as the displacement liquid for relatively large specimens. In this case the capillary should be at least 1.5 mm. in internal diameter to prevent the inclusion of minute air bubbles. With very small specimens the high surface tension of water causes errors due to the inclusion of air bubbles on the surface and between the particles of solid sample. The most satisfactory displacement liquid is ethyl ether but correct results are obtained only by careful attention to the proper method of using the apparatus. With ethyl ether any minute air bubbles adhering to the surface of the specimen may be readily liberated by



Device for Estimation of Density of Gems and Small Amounts of Solids

¹ Received September 19, 1930.