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 definit 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

known; and the float is calibrated by solutions of known concentration.[1]

The sensitiveness of the method is indicated by the following observation. A buoy-shaped or fish-shaped glass float, of not more than five cubic centimeters displacement, will distinctly change from floating to sinking when the temperature of the liquid is raised 0.001°, if just on the equilibrium point; and probably even a smaller temperature change would have an appreciable effect. This corresponds to a change of density of about 0.000001 in the case of most organic solvents, or about 0.0000002 in aqueous solutions. If a 1% solution of a salt has a specific gravity of 1.01 compared with water at the same temperature, this degree of sensitiveness should enable one to estimate the amount of salt present to within 0.002%.

A mercury thermometer used for this purpose is best calibrated with all possible care; but if the bore is very uniform and the graduation is perfectly spaced, the degrees need not correspond to any recognized scale. Good results may be got with any good Beckmann thermometer. Platinum resistance thermometers or multiple thermopiles may be used with advantage by those familiar with very exact electrical measurements, if they possess apparatus from which stray electromotive forces are rigorously excluded; in this case ohms or millivolts may be plotted directly against concentrations without translation into centigrade degrees.

A thermostat capable of being easily adjusted at any needed temperature and of being kept there within 0.005° is required in order that the greatest accuracy may be attained. There is no great difficulty in accomplishing this; an Ostwald toluene-regulator of large capacity and large surface is arranged to make electrical contact with a movable wire in its capillary. This capillary is graduated, and the adjustment of the wire needed for any given temperature is easily found. The current thus regulated operates a relay for a stronger heating-current, or any other intermittent heating device.

The solution to be investigated is placed in a liter Erlenmeyer flask, immersed in the adequately stirred thermostat, and the float within the flask is viewed by reflection in a small inclined mirror kept beneath the water of the bath.

The float should be small and shaped, as has been said, like a buoy or fish, or very plump cigar. It should be made several months before it is used, if permanency in calibration is desired, so as to allow the attainment of constant volume after the internal upheaval due to heat. A recently made float may be used temporarily; but it must be recali-

[1] Since this work was finished, Andreae has published a method of determining the density of minerals which has some similarity in principle to the method herein described. The form of apparatus and method of application are different, however. *Z. phys. Chem.*, **76**, 491 (1911).

brated with known solutions every few days. Approximate adjustment may be made by the addition of mercury or shot before sealing, and the final adjustment to any desired weight by adding glass to a short, thin, glass rod permanently attached to one end. Because the coefficient of expansion of the float as well as of the liquid enters into the effect, the results obtained with floats of different materials are not directly comparable. We have used common soft glass, Jena glass, and fused silica as the material for the float. The results given below were obtained with a float of common soft glass; but the best material is probably the standard thermometer glass, well known as Jena glass 59^{III}. We propose in the near future to publish results obtained with this glass.

The data of a single determination are recorded below in order to illustrate the method. In the first place, typical readings of a single setting may be given.

At 15.394° the float sank in the liquid.
At 15.390° the float rose in the liquid.
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Thus there was no question that the temperature could be fixed within 0.001°. It is not easy to attain the point where the float neither rises nor sinks, but this is not necessary; we contented ourselves usually with the narrowing of the range to within the small limit recorded above.

A series of measurements made by diluting 474.53 grams of alcohol of 98.99% purity by successive weighed additions of water, and taking the corresponding temperatures of floating equilibrium, is given below. The float used had been well seasoned, the temperatures were determined with the greatest care and referred to the international hydrogen standard, and all weights were reduced to the vacuum basis.

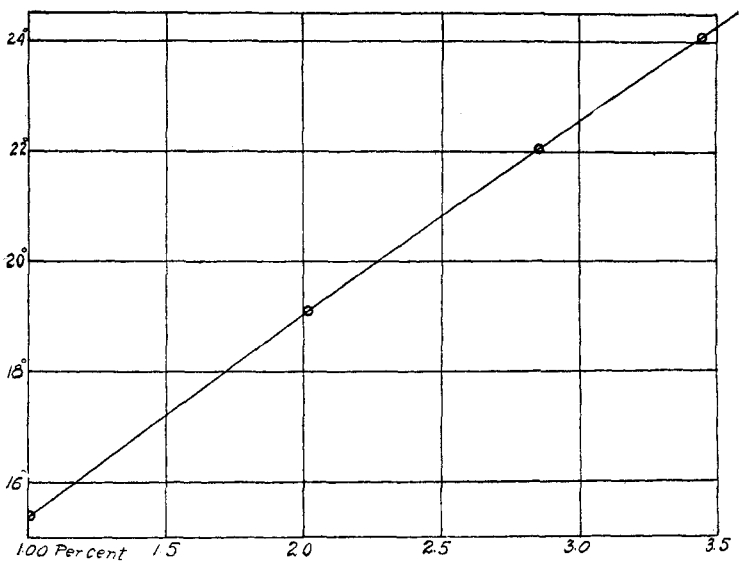
Water added (grams).	Per cent of water in alcoholic solution.	Temperature of floating equilibrium.
....	1.010	15.391°
4.8845	2.019	19.083°
4.1230	2.855	22.050°
2.9389	3.446	24.093°

Other series gave similar results, with curves exactly coincident when the start was made from the same concentration.

On plotting these results the following diagram is obtained, which must be drawn upon a very large scale to gain the full benefit of the accuracy of the method.

This curve may be used for the analysis by means of this float (or any other exactly similar float) of alcohol of any degree of purity between 99% and 96.5% (provided that water is the only impurity) as follows:

In one case, for example, a given specimen of alcohol was found to give floating equilibrium at 15.492°. Upon adding 9.550 grams of water to 375.77 grams of this alcohol, the floating equilibrium temperature became 24.251°. According to the curve, based upon the preceding table, these two solutions are found to contain 1.038 and 3.492% of water respectively. The difference between the two is 2.454. The



FLOATING EQUILIBRIUM TEMPERATURE AND CONCENTRATION.

Temperatures at which the float is in equilibrium with the solution are plotted in the direction of ordinates, and percentages of water in the diluted alcohol are plotted in the direction of abscissae. The curve is almost, but not quite, a straight line.

consistency of these results is seen from the fact that the difference as similarly calculated from the weight of water actually added is 2.453, assuming the first solution to contain 1.038% of water. The difference is only 0.001% of the total, or 0.04% of the added water. Many other similar experiments have been made with equal or even greater satisfaction, but they need not be recorded here.

Clearly the method is dependent upon the presence of only two components and demands for efficiency a decided difference between their densities. Where the densities are nearly alike and only trifling changes of volume occur on dissolving, the method is inapplicable.

For wide ranges of concentration one may use either several floats with different but overlapping ranges of operation, or else (less advantageously) a wider temperature range. It is evident also that the method may be used in a reverse fashion for standardizing thermometers by means

of known solutions. Thus, for instance, if a certain concentration of hydrochloric acid corresponds to a given temperature of floating equilibrium, and another equally definit concentration corresponds to another temperature, the difference between these temperatures can be fixed once for all by the mere titration of the two specimens of acid, and may be duplicated at any time with this float or one of the same density made from glass of the same coefficient of expansion. Such cases have been studied in detail and have been found to yield very satisfactory and interesting results. It is hoped before long to publish the somewhat voluminous data. For the present this preliminary paper will give an idea of the general problem and perhaps be of service.

It may perhaps be added that floats of this sort are of great service in preparing exact solutions (for example, in volumetric analysis) of predetermined density. In the present case, to cite a specific instance, alcohol of exactly 98.000% purity could have been made by setting the thermostat at 19.016° (read off from the curve) and adding water drop by drop to a purer alcohol until floating equilibrium was reached. For many years they have been used thus at Harvard to fix certain definit solutions at a fixed temperature.

Enough has been said in this paper to show that the method is one of considerable accuracy, and that it has a wide range of application to common problems of industrial as well as theoretical interest.

To recapitulate: it has been shown that the method of determining equality in density between a solid and a liquid by floating is applicable to a simple method of quantitative analysis, because the "floating equilibrium temperature" is an almost linear function of the concentration. Hence the reading of the temperature gives at once a determination of the concentration.

As this method is exceedingly sensitive, small changes in concentration may be detected with a degree of precision equaled by few other analytical processes. The process may be used either to determin concentrations by means of known temperature differences or else to determin temperature differences by means of known concentrations, when the relationships have been found once for all for any given substance. Thus it may be used not only to analyze solutions but also to calibrate thermometers, as well as to prepare exact solutions of any desired concentration. The coefficient of expansion of the solid float may also be determined with its help.

A more extended paper upon the subject in all its ramifications will be published in the near future. Much more work has already been done, and is almost ready to publish, and yet more is in prospect.

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