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A CONVENIENT METHOD FOR CALIBRATING THERMOMETERS BY MEANS OF FLOATING EQUILIBRIUM.

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In a recent paper entitled "A New Method for the Quantitative Analysis of Solutions by Precise Thermometry,"[1] the authors pointed out that the "floating equilibrium" of a suitably shaped solid float is a highly sensitive phenomenon, and that the floating equilibrium-temperature, with a given solvent and dissolved substance, is almost a linear function of the concentration. It was shown that this process may be used either to determine concentrations by means of known temperature-differences or else to determine temperature-differences by means of known densities or concentrations. Thus the method may be used not only to analyze solutions, but also to calibrate thermometers, and with previously standardized floats to fix thermometric points as well as to prepare exact solutions of any desired concentration.

The object of the present paper is to continue the discussion of this process, and especially to apply it to the often troublesome problem of standardizing thermometers with accuracy. This paper will soon be followed by others.

It is apparent that the point of floating equilibrium, at which a given float and the liquid in which it is immersed have the same density, must occur in a definite liquid at a perfectly definite place on the thermometric

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[1] THIS JOURNAL, 34, 599 (1912).

scale. By taking a suitable float and a salt solution, easily capable of exact analysis, the concentrations corresponding to a series of temperatures as read on the scale can be ascertained, and a concentration-temperature curve can be drawn on which any given temperature has a corresponding concentration. Thus by reproducing known concentrations and using a float with the same or nearly the same average specific gravity as that used in the original production of the curve, a thermometer previously uncalibrated could be standardized at any or all points on the curve. Moreover, even without a standardized float, irregularities in a thermometer, not previously calibrated, could be often detected from the lack of smoothness of the curve drawn through its readings.

These preliminary remarks show that the method holds out great promise of usefulness. In the work to be described, which is only preliminary in its nature, several forms and materials were used for the float, most of the experiments having been made with floats of fused quartz, or common German soft glass.

The method of experiment was precisely that used in the preceding portion of the research already described in the paper mentioned above.

The float should be small and shaped like a buoy or a fish. A sketch, giving an idea of the best shape, is appended. Such a float is easily changed from sinking to rising by a fall of 0.001° in aqueous solutions. An excellent thermostat is necessary if great accuracy is sought. Further details are given in the article already referred to.

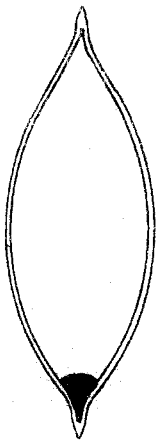
Fig. 1.

Aqueous solutions of sodium sulfate were selected as convenient bi-component systems, because the salt is easily obtained in a pure state, and the solutions are easily analyzed by evaporation.

The vessel used to contain the solution was an Erlenmeyer liter flask of Jena glass provided with a doubly perforated rubber stopper through which passed the thermometer and stirrer. This flask was immersed to the neck in the thermostat. In order to prevent evaporation from the surface of the solution, the stirrer was made to operate in a glass tube, through which was conducted a current of air saturated with vapor from a solution of the same concentration and temperature as that in the flask. This secondary solution was kept in a gas wash-bottle immersed in the thermostat, and a current of pure air was forced slowly through it and thence to the stirrer. This precaution prevented any evaporation even when the determination lasted over an entire day.

The thermometer was a very accurate one covering a range of 9° from 15.5–24.5°. It was standardized with great care by comparison with instruments carefully standardized at the Bureau International at Sevres.

The analysis was made by a method already used at Harvard[1] for determining sodium sulfate and silver nitrate. About 20 cc. of the solution were removed and weighed; the water was then evaporated and the anhydrous salt remaining was also weighed. An attempt had previously been made to carry out the evaporation in an open platinum basin heated in an oven, but this was found to be quite impracticable, because of spattering. Resort was then had to fused silica flasks of 0.05 liter capacity provided with long necks. Into these the solution was placed, and they were heated to about 103° in an electric oven, while a current of dry air was blown upon the surface of the solution in each. A glass tube, provided with a fused silica cap held in place by a platinum wire, conducted the air down the neck of the flask to within four or five centimeters of the surface of the solution. Any projected particles or drops adhered to this cap. After the water had been driven off, the temperature was gradually raised to 400° and kept there for over two hours, when experiment showed that constant weight was attained. The quartz cap was then detached and dropped into the flask, and after cooling in a desiccator over caustic potash, the flask with its contents was weighed, together with the cap and platinum wire.

An attempt was made to make the dehydration yet more certain by fusing the salt in the quartz flask. With great care this can be done, but the result was sometimes disastrous to the flask, the molten salt attacking the fused silica to a considerable extent. Accordingly, this extreme treatment was abandoned. The fairly constant quantity of water still retained by the salt dried at 400° was probably less than one part in ten thousand, but as it must have been approximately constant in different specimens, no correction was applied for this amount. The loss on fusion, found some time ago by one of us for dehydrated sodium sulfate, was 0.0003 gram from 3.30658 grams of the salt.[2]

The weighings were all made by the method of substitution on a Troemner balance, using standardized weights, and all weighings were reduced to the vacuum standard.

Considerable difficulty was experienced at first in weighing the quartz flasks. Sometimes two hours were needed for the attainment of constant weight, while on other days accurate weighing was impossible. The trouble was probably due, as usual, to three causes, namely, static charges of electricity upon the flask, inequalities in temperature, and humidity.

The first-mentioned difficulty seems to have been the most serious of the three, for after a very small tube containing impure radium chloride

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[1] Richards, *Proc. Amer. Acad.*, **26**, 258 (1891).

[2] Richards and Forbes, THIS JOURNAL, **29**, 813 (1907).

(1000x) was introduced into the balance case, no trouble was experienced in obtaining constant weight. In several cases, the amount of the combined disturbing effects was recorded, and may be of interest. For example, one of the quartz flasks was exactly balanced by counterpoise, and then taken off and rubbed vigorously with a cloth and immediately reweighed. It was two milligrams too light, and at the expiration of four minutes it was still deficient one milligram. At the end of fifteen minutes, it was five-tenths of a milligram less than the original weighing, and even at the end of thirty minutes it still possessed a slight charge. On placing the radium tube in the balance case, the original equilibrium was quickly restored.

After some preliminary experimentation, the best method of determination was found to be very simple. The sodium sulfate solution of a concentration needed to give "floating equilibrium" at approximately the desired temperature, was placed in the Jena flask together with three floats, and the flask immersed up to the neck in the thermostat. The final adjustment of the concentration was obtained by adding a few drops alternately from two solutions, one a little less and the other a little more concentrated in sodium sulfate than that in the flask. The exact floating equilibrium was attained by changing the temperature of the thermostat. The flask was corked and the current of saturated air from the auxiliary flask turned on. Without now altering the concentration, the temperature at which each floating equilibrium occurred was approached from either side, until rising and sinking were observed to be within two one-thousandths of a degree of each other, and the mean was taken as the true temperature in each case. The positions of the floats were reflected from a mirror immersed in the thermostat as already stated. The floats were, of course, studied one by one; when the equilibrium temperature of one float had been secured, the temperature of the thermostat was changed until a second float was in floating equilibrium, and finally the third. Then the redetermination of the first float indicated whether any accidental change in concentration had occurred during the operations. Before the device for preventing evaporation was adopted, considerable change was observed; for example, during five hours, the change in equilibrium-temperature, due to evaporation, was found in one case to be the hundredth of a degree, and this on standing over night increased to two-tenths of a degree. This loss of water was entirely prevented by using the auxiliary device mentioned above, not the slightest change in concentration being observed in this case, even when the atmospheric humidity was very low and operations extended over a long time. For example, during a determination made on May 16, 1912, at 19.5° (when the room temperature was 28.5° with about normal humidity) no change in the equilibrium temperature occurred during six hours.

On the completion of the trials, two samples of about 20 cc. each were removed by a pipet into the two previously weighed quartz flasks. These were then stoppered with glass stoppers and placed under a bell-jar. In order that any possible evaporation might be reduced to a minimum, a small dish containing a few cc. of the same solution was placed under the bell-jar with the flasks. After standing thus for at least an hour, the flasks and contents were weighed by counterpoise and then evaporated by the method already described.

Below is given a sample of readings made in one instance when ascertaining the exact "floating equilibrium" for float A. "Up" indicates that the float tended to rise, "down," a tendency to sink.

17.481 up
17.484 down
17.483 down
17.482 constant
17.480 up

These readings illustrate the sensitiveness of the floats to change in temperature. There could be no doubt that 17.482 was the temperature to be taken in this case. The floats were not all exactly equal in sensitiveness—doubtless both the size and shape of the suspended object influence the velocity of its passage through the solution.

The floats were weighed from time to time during the research in order to see if they remained constant in weight; for it was important to discover whether water might be absorbed by them, or whether they might dissolve in water. The following weights of the washed and thoroughly dried bulbs showed that they remained essentially constant. Of course, the absolute weight of the floats is of no consequence, but any change in weight during the investigation would have disastrous results.

Date.	A. Quartz.	C. Quartz.	D. Glass.
Jan. 11	5.42346	2.98863	4.84407
Mar. 11	5.42346	2.98842	4.84407
Apr. 11	5.42341	2.98847	4.84412

Thus none of these probably lost an important amount during the part of the research between March 7th and April 1st. The slight fluctuations may have been entirely due to changes of temperature, as no counterpoise was used in weighing. Other weighings, on March 15th and 29th, when no desiccating agent was used, gave values averaging about 0.1 milligram greater, due doubtless to adsorbed moisture.

Although these experiments were fairly conclusive, further experiments on a larger scale were made in order to determine if fused silica of the best quality is sufficiently porous to absorb water or salt solutions. Three flasks of fused silica were dried for some time at 200° and allowed to cool in a vacuum desiccator over caustic potash. They were then removed to an ordinary desiccator and weighed, one of the flasks being used as a counterpoise. The other two flasks were then immersed up to the neck in water; and after twenty-three days they were taken out, wiped dry, and left exposed to the air of the room for six hours. The counterpoise was dipped into water for a moment and wiped dry under identical conditions with the other flasks, except as to the length of time of immersion. No change in the relative weights of the flasks was found to have occurred. Hence the silica absorbed no water during its three weeks' immersion. This having been shown, the experiment was repeated, using a sodium sulfate solution containing 11% of the salt. The flasks were kept immersed in this solution for over a month and then washed and weighed. As before, no change in weight was found.

It appears safe, therefore, to conclude that the best quality of fused quartz does not absorb water or sodium sulfate to any appreciable extent when exposed to the action of these substances.

The densities of the floats were determined towards the close of the investigation. Float A was brought into floating equilibrium with the sodium sulfate solution at 20.003°. The density of this solution was ascertained in a large Ostwald pycnometer, of 0.05 liter capacity, provided with ground glass caps and the density of float A was thus found to be 1.10155 at 20°/4°.

From this value, and the appropriate coefficients of expansion, together with the curves to be shortly depicted, the densities of floats C and D were calculated to be 1.10151 and 1.10166. Dividing the weight of each float by its corresponding density, we obtain, as the volumes of the floats, 4.92344, 2.71307 and 4.39704 cc., respectively.

The cubical expansion for fused quartz is often taken as 0.0000018. This is so small as to affect its density only 0.00001 over the range of temperature (4.1°) covered in this research. Assuming the usual value of the coefficient of expansion of glass (0.000025), the volume of glass float D at the lowest temperature (15.9°) is found to be 4.39667 and the density 1.10177, instead of 1.10166, the value at 20°.

These preliminary data having been recorded, the data and curves which show the change of floating equilibrium temperature with concentration of the sodium sulfate solutions may be given. The experiments were begun in January, but the preliminary experiments were affected by the fact that the floats were new and had not attained equilibrium. Hence, for the present purpose these preliminary experiments may be omitted. In the near future we hope to present complete data concerning the slow alteration in volume exhibited by glass and fused quartz on standing as determined in this way; for the method lends itself with especial fitness to this test. The values tabulated are five sets of determinations made in March, 1911. These include all those made during that month except one determination which was vitiated by a known accident.

TABLE.—"FLOATING EQUILIBRIUM" TEMPERATURES OF FLOATS TOGETHER WITH THE CORRESPONDING CONCENTRATION OF SODIUM SULFATE.

Results.

Date of determination.	Float A.	Float C.	Float D.	$\frac{\text{Wt. salt}}{\text{Wt. solution}}$
Mar. 7	15.888	15.991	......[1]	0.109322 0.109319
Mar. 9	17.394	17.497	16.910	0.109887 0.109885
Mar. 22	18.408	18.509	18.025	0.110267 0.110267
Mar. 25	19.421	19.516	19.145	0.110670 0.110678
Mar. 28	19.968	20.068	19.729	0.110866 0.110858

The meaning of this table will be made more clear if a single determination is described. A certain solution of sodium sulfate containing nearly 11% of the anhydrous salt was made. On March 9th float A was in equilibrium with this solution under the precautions already stated at the corrected temperature 17.394°; float C at the temperature 17.497°, and the glass float D at 16.910°. When these temperatures had been satisfactorily determined, two portions of the solution were weighed out in quartz flasks. Of these portions, one weighing 20.1283 grams yielded 2.21184 grams of dried sulfate, and another weighing 20.1471 grams yielded 2.21387 grams of solid. The percentage of sodium sulfate present in the solution was thus found to be 10.9887 and 10.9885 by the two determinations, respectively, as given in the last column of the table. The difference between them corresponds to 0.04 milligram, which is about the probable error of weighing. Some of the pairs agreed more closely; others less closely, but it was clearly possible to determine the concentration of the solution with great accuracy. As already stated, the chief uncertainty lay in the question as to whether or not the salt was wholly dry, on account of the inexpediency of fusing this substance in a quartz flask. A platinum flask would have served better.

The results, when plotted with regard to concentration and temperature, give two almost linear parallel curves for the two quartz floats. The glass float also gives almost a straight line, but its greater alteration in volume with change in temperature is indicated by the increased slant towards the temperature axis as compared to the curves given by fused silica. The fact that these curves are so nearly straight is very fortunate as regards the application of the method to the calibration of thermometers; for very few points are needed to fix the line throughout its length.

The method of using either of these curves for standardizing a thermometer is as follows: The particular float chosen or one constructed of similar

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[1] Below the graduation of the thermometer.

material and of nearly the same average density, is placed in a solution of sodium sulfate maintained at the lower of the temperatures to be verified. A weaker or more concentrated solution of sodium sulfate is added at this constant temperature until the float is in precise floating equilibrium. Some of the solution is then removed and put on one side for analysis. Immediately afterwards the solution is warmed to the other end

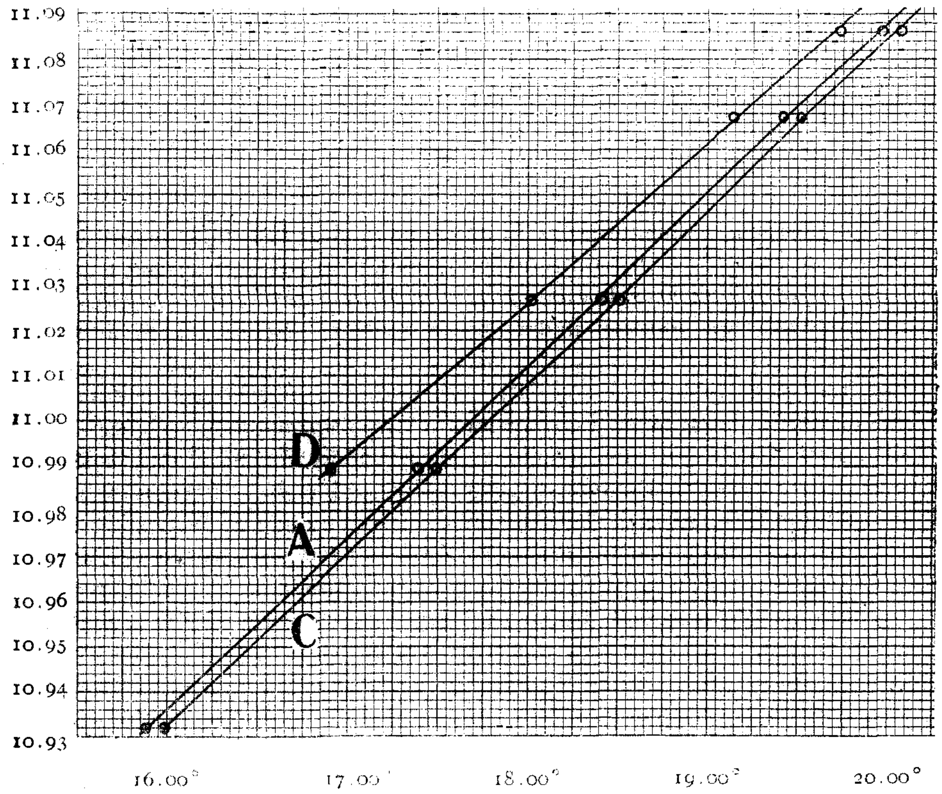

Fig. 2.—Curves showing relation of floating equilibrium temperature to concentration of solutions for three floats: A, C (silica) and D (glass).

of the temperature-interval under investigation; floating equilibrium is again attained by increasing the concentration of the sodium sulfate, and a new portion is taken out for analysis. The two points on the curve corresponding to these two percentage compositions of solution should give the true temperatures; and the corrections of the thermometer employed are simply found by subtracting its readings from the two values thus read off from the curve.

For example, let us suppose that with a given thermometer and a similar glass float, the temperature 17.200° was found to correspond exactly with

11.0000% of dissolved sodium sulfate, whereas the temperature 18.200° was found to correspond to 11.0325%. The temperatures (as found from a much enlarged curve or by interpolation) which ought to have corresponded to these concentrations were, respectively, 17.244° and 18.195°. Accordingly, the thermometer read 0.044° too low on the lower point and 0.005° too high on the upper point. Instead of being exactly 1.000°, the true temperature-interval was, therefore, the difference between the two last-given figures, namely, 0.951°.

Evidently, in order to attain the certainty of 0.001°, very great accuracy in analysis is necessary. A variation of 0.01° in temperature corresponds to only about 0.0034% of the weight of salt in the solution, or 0.06 milligram when only two grams are weighed. Of course, the curve as given above, is nothing but a preliminary one, and serves rather merely to exemplify the method than to act as a final standard of reference. The technique may clearly be much improved. The line, as drawn, is not perfectly smooth; the irregularity may be due either to an imperfect analysis of the solution taken from either of the two upper series of points, or to an error in the thermometer employed at one of these positions. Such irregularities are not inherent in the method but may be traced to their source through further experiment. For finality, many more determinations should be made with a number of thermometers standardized independently with the greatest care at the Bureau International, and, moreover, floats of definite materials should be employed so that the standard may be easily duplicated in any given locality at any given time. In the near future, experiments are to be made here with a variety of such floats, for example, of platinum, silver and glass of definitely known composition. Besides this, solutions of other substances, especially hydrochloric acid, are to receive attention.

Nevertheless, even without further knowledge, a single curve of this sort may be useful in comparing one part of a given thermometer with another part, or in smoothing out irregularities in a curve giving its corrections. If a smaller degree of precision, than that aimed at in the present work is sought, the analysis may be carried out volumetrically, and the problem becomes vastly easier.

It is evident that, when the locus of a given curve over a definite interval has been once for all obtained, any similar float may be standardized by means of a very few points. For example, if a small range were concerned, the two points recently found at Harvard for the transition temperatures of sodium chromate, namely, the decahydrate-hexahydrate, 19.525°, and the decahydrate-tetrahydrate, 19.987°, might be used; or for a larger range these points in conjunction with the transition temperature of sodium sulfate, 32.383°.

If sufficient care is employed, this method may also be used for determining the coefficients of expansion of liquids with known floats, or coefficients of expansion of floats with known liquids. Therefore, any substance which may be made into a float may profitably be studied as to its coefficient of expansion in this way; and such studies will be made in the near future in the Wolcott Gibbs Memorial Laboratory.

The authors take pleasure in expressing their gratitude to the Carnegie Institution of Washington for generous help in the prosecution of this work.

Summary.

In this preliminary paper, experiments are described showing how the phenomenon of floating equilibrium may be used to standardize thermometers. The method consists in determining the temperatures, at which different analyzed solutions of a given substance attain exactly the density of a given float. When the almost linear curve, showing the relation of this floating equilibrium-temperature to percentage composition, has once been established, it will serve for the calibration of any thermometer at any time.

The use of the method as a convenient means of determining the coefficients of expansion of liquids with known floats, or coefficients of expansion of floats with known liquids is also indicated.

Further work upon the subject is now being prosecuted in the Wolcott Gibbs Memorial Laboratory of Harvard University.

[Contribution from the Chemical Laboratories of New Hampshire College.]

THE DIMETHYL PHOSPHATES OF THE RARE EARTHS.

By J. C. Morgan and C. James.

Received November 8, 1913.

The study of methods for the separation of the rare earths, and of new compounds of the rare earths that seem likely to be of use for such purposes, has, for a long time, occupied the attention of those interested in this branch of chemistry.

The rare earth salts of dimethyl phosphoric acid seemed, on preliminary investigation, to be possessed of properties which would make dimethyl phosphoric acid an extremely valuable reagent for the separation of some of the rare earths. Therefore, a study of the properties of these compounds was commenced.

This investigation involved the preparation of dimethyl phosphoric acid; the preparation of the rare earth compounds from this; the determination of the composition and solubility of these compounds; and finally several fractionations of rare earth mixtures.

Preparation of Dimethyl Phosphoric Acid.—This acid was prepared, according to the method of Hugo Schiff,[1] by allowing methyl alcohol to

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[1] *Chem. Centralblatt*, **1857**, 761–763, 864.