[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

FURTHER STUDY OF FLOATING EQUILIBRIUM.

BY THEODORE W. RICHARDS AND GORHAM W. HARRIS

The use of floating equilibrium in determining specific gravity was perhaps first suggested by Davy, in his work on the density of the alkali metals. Pisati and Reggiani[1] are credited with having used the method for studying liquids for the first time. In two recent preliminary papers[2] it has been shown that the exceedingly sensitive floating equilibrium of a suitably shaped float suspended in a solution of the same density may perhaps be capable of a variety of useful applications—on the one hand, to methods of chemical analysis, and on the other, to the calibration of thermometers, as well as to the study of the coefficient of expansion of the float or the liquid. The method has the virtue of being comparatively simple and inexpensive, thus being within the reach of almost anyone.

This being the case, a careful study of the especial precautions necessary for the exact prosecution of such work becomes important, and the present paper describes very briefly further experiments concerning: firstly, the precautions necessary for quick and accurate determination of the floating equilibrium; secondly, the thermal hysteresis of glass floats; thirdly, the effect of changing atmospheric pressure upon their behavior; fourthly, the effect of traces of common impurities in water; and finally, the temperatures of floating equilibria of the floats in various dilute solutions of hydrochloric acid, which afford a means of analyzing the solution or of standardizing approximately a given interval in a thermometer. Hydrochloric acid was selected as a standard substance because of its ready purification and the ease with which its solutions may be analyzed by volumetric methods. The outcome shows, as usual, that the attainment of accuracy demands thought and care; but also that useful and interesting results may be obtained with due precautions.

Apparatus and Precautions.

A thermostat capable of maintaining a constant temperature within one-thousandth of a degree and of easily altering this constant temperature at the operator's will is essential for great precision. Some such a contrivance may with advantage be at the disposal of anyone who wishes to standardize a thermometer by any method.[3]

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[1] Pisati e Reggiani, *Rend. R. Acad. d. Lincei*, [4] 7, 99 (1890).

[2] Richards and Shipley, THIS JOURNAL, 34, 599 (1912); 36, 1 (1914). Attention is called also to the interesting, accurate and valuable work of Lamb and Lee, who balanced increased bouyancy by magnetic attraction. THIS JOURNAL, 35, 1666 (1913).

[3] See, for example, the chapter by one of us in Stähler's "Handbuch," Vol. III, p. 259 (1912). By arranging the platinum contact point so as to be movable over a fixed scale, the shifting of the temperature is easily effected.

The method was essentially that described on page 2 of our paper of 1914.[1] The hydrochloric acid solution, in which was suspended the fish-shaped float, was protected from evaporation by a current of properly moistened air, and provided with an efficient stirrer to promote rapid adjustment of temperature. This stirrer must have a smooth bearing; if it consists of a glass rod running through a glass tube, enough glass powder may be ground off to influence appreciably the density and, therefore, the floating equilibrium temperature of the solution, even in a single day. To overcome this difficulty bearings were made of platinum foil at each end of the tube admitting the stirrer. A collar of platinum foil was slit above at intervals, and the strips bent outwards and over, and fastened here and there by means of fusible glass. With this arrangement, although traces of platinum dust were worn from the bearings, no glass was worn away, and the solution in the flask remained intact.

The floats, of the fish shape previously described, were observed by means of a small, inclined mirror outside of the flask but immersed in the water of the thermostat, and marks on the side of the flask helped to show whether the float was rising or sinking. Great pains must be taken to prevent small air bubbles from attaching themselves to the float.

Four kinds of glass were used in the floats: soft German tube, Jena tube with the red line called "Durorobax," Jena reagent glass, and the American "Nonsol." Mercury is the most convenient material for ballast.

Such floats remain constant in weight over a long period,[2] but their changes of *volume* soon after preparation are, however (as was suggested in one of the previous articles),[3] highly important. At that time no quantitative determination was made. Accordingly, two floats were now tested in pure water over a long period from the day of their preparation, the results being given in Table I and plotted in Fig. 1.

TABLE I.—CHANGE OF FLOATING EQUILIBRIUM TEMPERATURE DUE TO CONTRACTION OF GLASS ON AGING.

Series 1.		Series 2.	
Age of float. Hours.	Float. equil. temperature.	Age of float. Hours.	Float. equil. temperature.
7	20.410°	2	19.884°
168	20.304	6	19.852
199	20.293	24	19.807
243	20.280	55	19.786
384	20.262	75	19.770
1632	20.1825	174	19.732
1687	20.1825	292	19.690
1752	20.1815	816	19.602
Total change,	0.2285°		0.2820°

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[1] *Loc. cit.*

[2] Richards and Shipley, THIS JOURNAL, 36, 5 (1914).

[3] *Ibid.*, 34, 600 (1912).

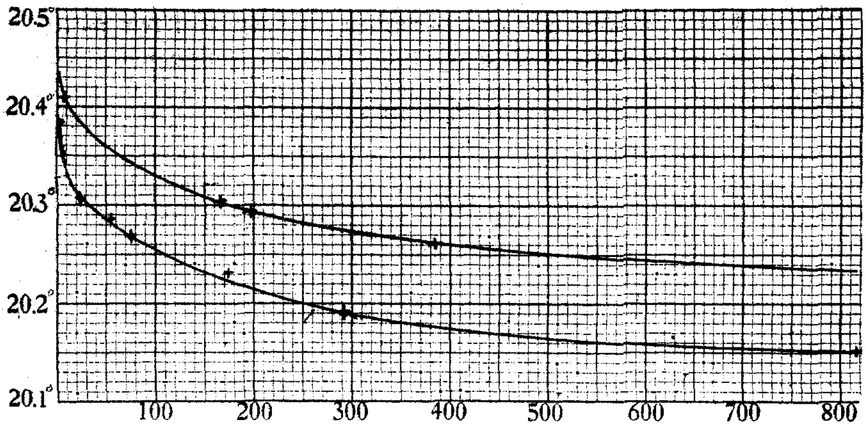

FIG. 1.—CHANGE IN FLOATING EQUILIBRIUM TEMPERATURE WITH AGE OF FLOAT. Temperatures are plotted as ordinates, times in hours as abscissae.

The contraction in volume suffered by the floats, in the first few hours of their existence, was very serious, and even after two weeks they were still considerably decreasing in volume, from week to week. This emphasizes the caution advised in a previous paper that the floats should be old. After two months, however, the change is very slow. The latter part of each of these curves is almost exactly logarithmic, and can be, therefore, extrapolated. When this is done, it becomes clear that after three or four months the floats must be altering so slowly in volume as not to affect appreciably any ordinary use to which they might be put within a moderate interval of time. More change of volume happens within the first week of the life of a float than in all the rest of its existence put together. The total changes (corresponding to 0.2° or 0.3° in the floating equilibrium temperature) are of the order of 0.005% of the volume. This is, of course, about the order of the changes measured by the rise of the zero point of a mercury thermometer after aging. Doubtless, also, similar but far less marked changes in the volumes of the floats occur because of less violent heating or cooling; hence, for the most accurate work it is important that the floats should have been previously kept at about the temperature of the room for a long time.

The floats were washed thoroughly, and thereafter handled only with glass, double-pointed, curved forceps.

During early trials, rapid agitation of the solution contained in the insulated receptacle was found to cause electrostatic effects, which gave irregularities at first incomprehensible. The trouble was naturally most prominent when the stirrer was lifted above the surface and quickly plunged beneath it, carrying air beneath the surface. Perhaps this trouble was the cause of the irregularity in a curve noticed in one of the preceding communications. When, however, the stirrer was always kept below the surface of the solution, and a grounded platinum wire dipped into the liquid, no further trouble was experienced. Negative results obtained in air from a special bulb prepared with a sealed-in platinum wire showed that the electrical charge *within* the float, due to friction of mercury, must be very small.

Preparation of Materials.

The substances used in the work to be described were prepared with care. The water used for all solutions had been three times distilled, once from alkaline permanganate, and once from dilute sulfuric acid. In almost all cases it was used within twenty-four hours of the last distillation, and was kept in borosilicate glass flasks. That it remained constant for a long time when thus preserved was shown by the fact that the floating equilibrium temperature in water which had been preserved in a stoppered borosilicate flask for two months was found to be exactly the same as that in the freshly prepared water. Thus the amount of glass dissolved in two months was too small to be detected, even by this very sensitive method.

"Chemically pure" hydrochloric acid diluted to about 20% was distilled through a quartz condenser, and the first third of the distillate discarded. The pure middle portion was at once diluted with purest water about half strength and kept in paraffin-lined bottles.

The sodium hydroxide used for titration of the acid solutions was freed from carbon dioxide by usual methods and was kept in paraffin-lined bottles protected from carbon dioxide.

The Effect of Dissolved Paraffin and Air on the Floating Equilibrium Temperature.

The solubility of paraffin in water might seriously affect a method so sensitive, hence its amount was approximately estimated. Very pure water, which had been kept in a paraffin-lined bottle for nearly three months, when evaporated in platinum left a volatile residue (doubtless paraffin) of 0.9 mg. and only a negligible weight of nonvolatile impurity. The conclusion that such a weight of this impurity (having a density near that of water) was not important was confirmed by experiments comparing the floating equilibrium temperatures of fresh water, and of similar water which had been stored for ten weeks in a paraffin-lined bottle. The temperature with the latter was found to be 0.0005° below the former, but this is about the limit of accuracy of the method. Hence the amount of paraffin dissolved by a liter of water has an effect on its density so slight as not to alter appreciably the floating equilibrium temperature, which would be perceptibly affected (to the extent of 0.001°) by a change of density of about 0.0000001.

The effect of dissolved air on the density of water and of the dilute solutions employed might also affect the floating equilibrium temperature. No difference, however, could be detected in the following trials, which were all carried out in a single day under constant pressure. The results follow:

Temperature with air-saturated water	20.1825°
Temperature with water freed from air by boiling and freezing	20.1825°
Temperature with the same water shaken with air	20.1825°

This is not very different from the result of Marek, who found at 21° (extrapolated) no appreciable effect in the seventh decimal place by saturating water with air. At 20°, on the other hand, he found a decrease of density thus caused of 0.0000004, which would correspond to about 0.003° in the floating equilibrium temperature. This latter amount could be easily and certainly detected. Hence we are inclined to think, because we observed no change whatever, that Marek's change of 0.0000004 in the density of water at 20°, due to the saturation of air, is too large, and should be nearer zero. It is perhaps worth noting that Chappuis[1] found an average value, between 5° and 8°, about 0.00000035 less than Marek's over this range. If this same correction is applied throughout Marek's work, his result would correspond very nearly to ours. Undoubtedly, if the percentage of dissolved carbon dioxide varied greatly, differences would be observed. Our experiments were made with air under usual conditions, which are fairly constant.

Analysis of Solutions.

Ordinary volumetric analysis being too crude for so exact a process, our solutions were analyzed titrimetrically by means of weight burets, consisting of 0.1 liter Jena flasks fitted up like miniature analytical "wash-bottles" with long outlets, and provided with capillary jets. Methyl red was used as the indicator, and sufficient precautions were taken to exclude carbon dioxide. It was ascertained that the accuracy attained was adequate for the problem in hand. A permanent solution was used for comparison of the end point, made of a very dilute solution of potassium dichromate and cobalt chloride in hydrochloric acid so prepared as to match exactly the tint of methyl red in a solution known to be neutral.

The Effect of External Pressure.

The effect of changing pressure upon the density of water is well known, but the similar effect upon the glass float cannot be predicted beforehand because this depends upon the quality and thickness of the glass as well as upon the shape of the float. The correction, therefore, must be empirical, like the similar correction applied to the thermometer, which also must be taken into account. This later effect, as carefully determined,

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[1] "Trav. Bureau Int.," 14D (1910).

varied with different instruments between 0.0022° to 0.0029° for one cm. of mercury.

Obviously, increase in barometric pressure by compressing the liquid tends to raise the equilibrium temperature, but, on the other hand, by compressing the float tends to lower the equilibrium temperature, and the net correction is the difference between these two effects.[1]

This net correction was found experimentally, partly from readings taken at different times when the barometer was fluctuating, and partly by artificially altering the pressure.

TABLE II.—EFFECT OF PRESSURE ON FLOATING EQUILIBRIUM TEMPERATURE (CORRECTED FOR EFFECT OF PRESSURE ON THERMOMETER).

		Corr. per mm.
Float I	Soft glass	—0.00041°
Float J	Jena reagent glass	+0.00006°
Float M	Jena reagent glass	±0.00000°
Float K	Durorobax glass	+0.00002°

A negative correction indicates that the float was less compressible than the water, and a positive that it was more compressible than the water. Except in the case of the large, thick-walled float of German glass, I, it is seen that the net effect is almost nothing at all, the two corrections counterbalancing one another, that is, the average compressibility of a thin-walled float of 7 cc. volume may be made very nearly equal to that of water. The larger thin float employed by Lamb and Lee was much more compressible.

Thus the effect of pressure must never be forgotten in work of this kind. Obviously a somewhat compressible float is more suitable than a highly incompressible one, as the net correction is then smaller; moreover, even the difference in pressure between the top and bottom of the flask may have a serious effect upon the equilibrium of a very thick float. Such a float as Float I had its floating equilibrium temperature altered 0.003° in 20 cm. depth of water, so that when the flask is at equilibrium temperature with the float at the middle, the solution on the top was 0.0015° above the equilibrium temperature at that point, while that at the bottom was the same amount below. The float would, therefore, remain suspended in the middle and not be very sensitive to changes of temperature. Much more sensitive results are obtained with a float thin-walled enough to approach in compressibility that of the liquid.

The Thermometers and Temperature Scale.

The thermometers used were instruments of high grade, partly Beckmann thermometers, and partly thermochemical thermometers made to cover the range between 15° and 20°, as well as two instruments of larger range; and they were verified by reference to Baudin instruments which

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[1] See Lamb and Lee, *Loc. cit.*, p. 1676.

had been very carefully standardized in Paris and elaborately studied here. They were thus all referred to the international hydrogen scale as exactly as possible under the circumstances.

Relation of Floating Equilibrium Temperature to Concentration with Hydrochloric Acid Solutions.

The method was extremely simple. The temperatures of floating equilibrium of the several floats in pure water in the neighborhood of 15° or 16° were first determined. Hydrochloric acid in definite amount was then added, and the temperature of the thermostat raised in steps until the exact floating equilibrium temperature of each float was successively reached; afterwards more hydrochloric acid was added, and so on. The amounts of added hydrochloric acid were often chosen so that the temperature would rise nearly a definite fraction of a degree. In each case portions of the hydrochloric acid were removed and carefully analyzed.

The main factors determining ease in detecting the equilibrium point are high coefficient of expansion and low viscosity. Alcoholic solutions, such as were described in the paper of 1912, are therefore especially favorable. The method works much less rapidly in a very dilute aqueous solution at 16° than in either of the solutions described in the previous papers; hence the present case is an unusually exacting one. Nevertheless there was no difficulty in securing the end point of floating equilibrium within 0.0005° if sufficient patience was employed. If, as is often the case, an accuracy within 0.01° is all that is required, the operation is much quicker and more convenient. Ordinary volumetric analysis is then sufficient, and the end point can be very quickly determined, because of the quick rising and falling of the float within the wide temperature limits permitted. Many of the precautions and corrections required in the more exact work become unnecessary. For example, the difficulty from currents produced by agitation or convection is scarcely noticeable, and the effect of changed barometric pressure on the float and solution becomes negligible.

The floating equilibrium temperatures of the five floats in several concentrations of pure dilute hydrochloric acid are given in Table III.

TABLE III.—EQUILIBRIUM TEMPERATURES AND CONCENTRATIONS.

Float J (Jena).	Float M (Jena).	Float I (soft glass).	Float K ("Durorobax").	Float L ("Nonsol").	Conc. of HCl (per cent by weight).
15.172	....	14.823	14.962	15.387	0.00000
16.178	15.776	15.953	15.996	16.412	0.02825
17.080	16.696	....	....	....	0.05547
18.093	17.730	18.051	17.961	18.344	0.08874
19.064	18.725	....	....	....	0.12282
19.925	19.599	....	19.827	....	0.15475
24.698	24.464	25.025	24.671	....	0.36368
....	....	....	32.362	....	0.79457
....	32.337	....	....	....	0.80833

The portion of these data between 14° and 20° is indicated by the five upper curves on the accompanying diagram (Fig. 2). The higher points were not included in order not to diminish too greatly the scale, but they lie on smooth curves continuing those given. The lowest curve represents the beginning of curve K, magnified tenfold.

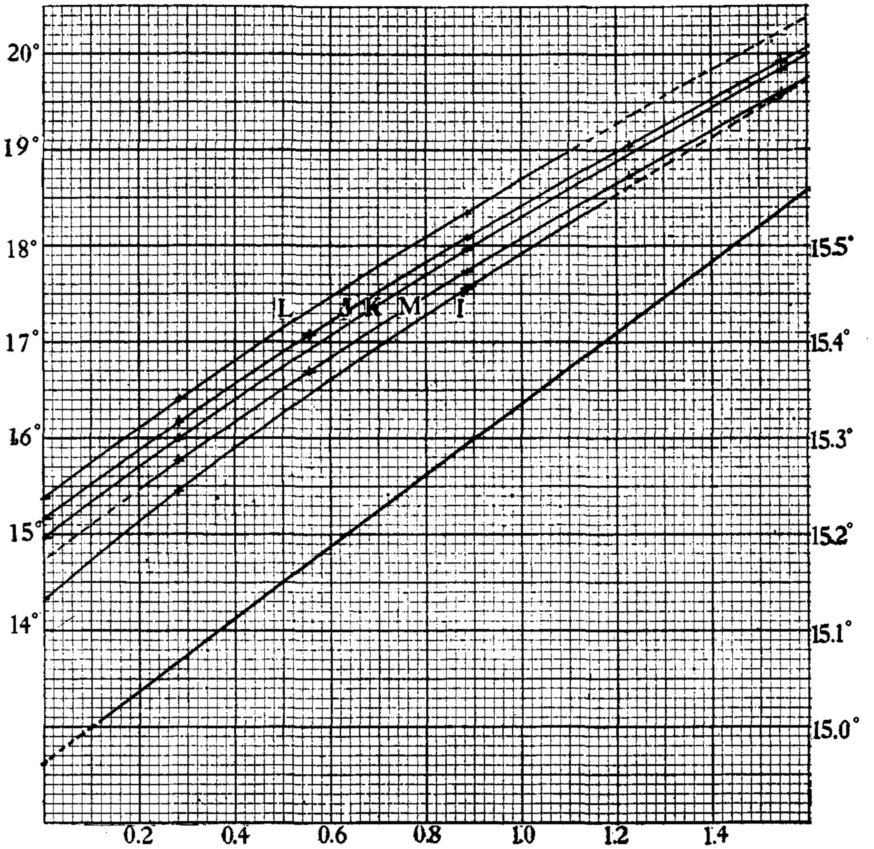

Fig. 2.—Floating Equilibrium Temperatures in Dilute Hydrochloric Acid.

Temperatures are plotted as ordinates, concentrations of hydrochloric as abscissae. The left-hand temperatures refer to the five uppermost curves, the right-hand only to the lowest curve. The abscissae numbers refer to grams per liter on the five upper curves, and decigrams per liter on the lowest. J and M are with reagent Jena glass floats; I, common soft glass; K, "Durorobax;" L, "Nonsol." In plotting 0.500° has been subtracted from each temperature in the case of Float I, so that its curve would not conflict with the others. The lowest curve is a ten-fold enlargement of the first part of K. The five upper curves, of course, are not on a scale large enough to show the full possibilities of the method.

Let us consider first the group of the five uppermost curves. All these curves, of course, are slightly convex upward, because the coefficient of expansion of water increases with the temperature; the greater the coefficient of expansion of water, the smaller is the rise of temperature necessary to counteract a given change in density due to added hydrochloric acid. The departure from a straight line is greater here than in the cases studied before. The lowest curve (I), representing soft glass, is steeper than the others, because the coefficient of expansion of soft glass is greater than that of the borosilicate glass. The difference in slope would obviously give a means of computing the difference in the coefficients of expansion. The other four curves are not far from parallel; thus the three varieties of borosilicate glass have approximately the same coefficients of expansion. Curves J and M both represent Jena reagent glass. They converge slightly toward the upper corner; a part of this convergence is due to the greater coefficient of expansion of water at the higher temperature, but this will not account for quite all of the effect. The two samples must therefore have differed slightly in coefficient of expansion. This is unfortunate, because it seems to indicate that each float must be standardized for itself; even a glass reputed to be of constant composition is not sufficiently definite to give precisely similar results with this very sensitive method, using different samples. Because of this limitation, it is hardly worth while to give equations of the type $n = at + bt^2 + ct^3$ for the curves, although if one wished to do much work with a single float this would be advantageous. The curves are to be regarded rather as typical than as universally applicable. Nevertheless, since the curvature is of necessity similar in the different cases, these curves may be of use to others in subdividing an interval when the two terminal temperatures are known, with any float of borosilicate glass.

The most obvious use for such curves, as previously stated, lies in the means which they afford of analyzing solutions with the help of a standardized thermometer. When no other more convenient means of analyzing the solutions exist, the method might be very useful in investigations demanding many determinations of the same type. Even if one has not a standardized thermometer at hand he can, nevertheless, use curves of this sort, provided that his thermometer is calibrated with reference to itself, or has an even bore; but of course in such a case his curves would correspond only to that particular thermometer.

The lowest curve in the diagram (Fig. 2) records the beginning of the curve with "Durorobax" glass magnified tenfold; here the unit of the abscissa numbers represents a concentration of 0.1 g. per 1000 g. of solution. Because of the possibility that the increasing appearance of the hydroxyl ion at very great dilution may affect the curve,[1] more data

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[1] Lamb and Lee have pointed out the remarkable effect of hydrolysis on very dilute sodium carbonate solutions. The possible effect referred to above is somewhat analogous (*loc. cit.*).

than those now presented will be required to fix this enlarged curve with complete accuracy at its lower left-hand corner, but it will serve for the present to exemplify the possible usefulness of the method with very dilute solutions. Such a single curve might be made applicable to many other substances besides hydrochloric acid, as follows:

In the first place, solutions of most substances as dilute as those covered by this curve must have very nearly the same coefficient of expansion as pure water. This inference is drawn from the data concerning the coefficients of expansion:[1] because it appears that the change in the coefficient of expansion of dilute aqueous solutions is nearly linear with the concentration, interpolation between concentrations of perhaps 1% and zero may be made with confidence; and one concludes that all solutions within this range must have a coefficient of expansion within a fraction of a per cent. of that of pure water. Hence this curve becomes not only a curve referring to hydrochloric acid alone, but also (within this range of error) to many other substances. The relation between different substances would thus become only a question of the density of the solution, and the curve would thus become a means of measuring density by means of the thermometer. Even if the hydrochloric acid has an irregularity at very great dilution, salt solutions from strong acids and bases have not (Lamb and Lee) and one of these would certainly serve if an acid would not. At this temperature a solution of hydrochloric acid which contains 0.1 g. of hydrochloric acid per 1000 g. has been found to have (again by interpolation between the almost linear larger concentrations and zero) a density almost exactly 0.000050 greater than pure water. To use the curve with any other specified substance one would need only to multiply the figures for hydrochloric acid by a proportional factor corresponding to the special salt. For example, one-tenth of a gram of sodium hydroxide per kilogram changes the density by 0.000115 or 2.30 times more than the same weight of hydrochloric acid. In order to reduce the figures as given for hydrochloric acid to those corresponding to sodium hydroxide, it would be, therefore, necessary only to divide them by 2.30. These figures are calculated from the known densities of the corresponding solutions as found by others. This extension of the method, now tentatively suggested as possible, deserves further trial and will be experimentally tested in the near future.

The manner of using curves of this sort for standardizing a thermometer has been already recorded in one of the previous papers.[2]

The present work has not yet brought any of this work to the stage of finality, but it confirms the conclusion of the previous papers that, because of the extreme sensitiveness of the indication of floating equi-

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[1] For example, see Landolt and Börnstein, *Tabellen*, 1912, p. 338.

[2] This Journal, 36, 9 (1914).

librium, the method may be one having many uses if the experimenter takes due precautions. Of course this method like many other phenomena concerning change of temperature cannot without great care, at least in its present stage, be depended upon to yield results as accurate as its readings are sensitive, chiefly because of the irregularities of the glass float. Anticipated work with a float of pure metal, which would be expected to be free from thermal hysteresis and would have a definite coefficient of expansion, has had to be postponed because of the difficulty of preparing such a float, but this task has been completed and in the future it is hoped such a float may be tested. Doubtless it would give more constant results than those described above.

We are glad to acknowledge our indebtedness to the Carnegie Institution for some of the apparatus used in this research.

Summary.

The solubility of paraffin in water has been examined and shown to be very small. For many purposes the use of paraffin-lined bottles as containers for standard solutions is, therefore, recommended.

Several newly described precautions, necessary for very exact work with floating bulbs in determining floating equilibrium, are recorded, and the effects of electrostatic charge, of varying pressure on liquid and float, and other possible causes of error were studied in detail.

The slow contraction of glass after fusion has been studied over a long range. This is a very important possible source of error in work of this kind, as suggested in the earlier papers.

Air dissolved in water at 20° has been shown to affect the density of water by less than 0.0000002.

Concentration-temperature curves have been studied with several floats made of different kinds of glass in dilute solutions of hydrochloric acid.

Such curves may be used for analyzing such hydrochloric acid with the help of similar floats and a standard thermometer, or for subdividing intervals of an uncalibrated thermometer. Until floats of perfectly definite composition are obtained, however, results for any one float cannot safely be used with another without preliminary testing on both ends of the range employed.

Because of the almost identical coefficients of expansion of very dilute solutions, the beginnings of such a curve may perhaps be used for many other solutions besides hydrochloric acid; it becomes a curve connecting approximately the density of any very dilute solution with the temperature of floating equilibrium. Thus one can determine densities thermometrically. The method will probably be more useful with such dilute solutions than with any others, but one must be on the lookout for the change in the concentration of the hydroxyl ion in extreme dilutions of an acid.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

SEPARATION OF THE METALS OF THE TIN GROUP.[1]

BY J. M. WELCH AND H. C. P. WEBER.

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The customary methods for the separation of arsenic, antimony and tin for qualitative purposes depend, in principle, either on the relative strength of the acids of these elements (for instance, the ammonium carbonate separation of arsenic from antimony and tin), or upon the difference in the solubilities of their sulfides in acids.[2] Of these principles the latter is perhaps the one most made use of in present practice.

Thus, in the procedure outlined by A. A. Noyes and W. Bray,[3] the three elements are separated from each other by the use of graded concentrations of hydrochloric acid. In the hands of a practiced operator this method leaves little to be desired, and is one of the most satisfactory methods described. When, however, the method was employed by persons of less manipulative expertness, such as students entering for the first time into qualitative work, the results were by no means as satisfactory as might have been anticipated. The statistics collected[4] show tin as giving the greatest trouble, it being missed in 20.2% of the cases considered. Arsenic was overlooked in 18% of the cases, while antimony was very rarely missed (less than 1%).

According to the method of Noyes, the sulfides of the second group are precipitated and then separated by treatment with ammonium polysulfide in much the usual manner, As_2S_5, Sb_2S_5 and SnS_2 being thrown out from the resulting polysulfide filtrate upon acidification with hydrochloric acid. Up to this point no particular difficulty is encountered, except occasionally with copper, which dissolves to a slight extent in ammonium polysulfide. This will be referred to again under the description of the new procedure.

The precipitated tin group sulfides, superficially dried, are then treated with exactly 10 cc. of concentrated hydrochloric acid (sp. gr. 1.20), and warmed for 10 minutes on the steam bath. Arsenic sulfide remains

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[1] Presented as thesis for the degree of B.S. by J. M. Welch to the College of Liberal Arts and Sciences, University of Illinois.

[2] A separation based upon the precipitation of antimony as the pyroantimonate of sodium has been proposed by Hahn, *Z. anorg. Chem.*, **92**, 168 (1915).

[3] THIS JOURNAL, **29**, 137 (1907).

[4] From reports of the students in qualitative analysis first semester 1914–1915. About 200 reports were examined.