

temporary hardness, due to the heavy, gritty sediment formed by freezing out the half-bound carbon dioxide. When, as is frequently the case, the impurities in a raw water are chiefly of this nature, softening with lime reduces the offending substances so much that it is often possible to produce first quality ice without core pumping, provided the air agitation is not stopped too soon.

Even when the presence of large amounts of impurities other than temporary hardness, or when improper air agitation prevents entire elimination of core pumping, lime-soda softening reduces the quantity of water that must be pumped. Usually one small core pumping is all that is required. This effects a very material saving in water and refrigeration, and, in a large plant, of labor. The freezing time is also shortened, increasing the plant's output.

CHECKING AND CRACKING

A very unwelcome and expensive phenomenon in an ice plant is the tendency of the ice to crack and shatter, particularly when low brine temperatures are employed. There has been no satisfactory explanation advanced for this tendency, beyond that the ice is evidently frozen under an internal strain.

It would appear to be quite possible that the presence of bicarbonates in the water is chiefly responsible for this strain. During the freezing process, while the half-bound carbon dioxide is trying to escape, the ice continues to crystallize, entrapping bubbles of gas and particles of the precipitated compounds, which are readily visible. The ice thus formed is comparable to a metal casting full of blowholes and impurities, and is in consequence inherently weak and brittle.

Some weight is given this hypothesis by the general experience that removing the bicarbonates of calcium and magnesium from a water by treatment with lime results in the production of much clearer and firmer ice, and frequently permits the use of lower brine temperatures. Further, in a recent series of experiments, ice was frozen from water to which had been added varying amounts of sodium bicarbonate. In all cases except the lowest concentration (10 grains per gal.) the ice formed was quite brittle, cracked readily, and showed considerable evidence of a bubbly structure. Analysis of the melted core ice showed the conversion of the bicarbonate to the normal carbonate in all cases to the extent that the normal carbonate alkalinity averaged 35 per cent of the bicarbonate alkalinity.

ZEOLITE SOFTENING

It is this relation of bicarbonate alkalinity to brittle and bubbly ice which is probably partially responsible for the unsuccessful application of zeolite softening to the manufacture of raw water ice. Contrasted with the actual removal of the bicarbonates of calcium and magnesium that is effected by softening with lime, the zeolite or base exchange process leaves in the treated water the slightly greater equivalent weight of sodium bicarbonate. Calcium and magnesium sulfate are converted to sodium sulfate, which has the disadvantages already discussed. Iron, silica, alumina,

and organic matter are not eliminated or reduced by zeolite softening.

LIMITING SALT CONCENTRATIONS

Finally, the question arises as to the limiting quantities of the various impurities that a raw water can carry and still make first-quality ice. We do not know exactly as yet, in all instances. Obviously, in the cases of the bicarbonates of calcium, magnesium, and iron, the limiting concentrations are their own solubilities, since softening with lime leaves the same residual content regardless of the initial concentration. It is also probable that the permissible maximum of silica and alumina is not exceeded in natural waters, if treatment with lime is employed.

With regard to sodium salts, and to calcium sulfate and chloride, investigations are now under way as to the limiting concentrations possible, and the results will be published when completed. Tentatively, it would appear that when the total soluble salt content of a raw water exceeds 30 to 40 grains per gal., exclusive of the temporary hardness, first-quality raw water ice cannot be made even with softening and high-pressure air agitation.

NOTE ON PARTIAL AND TOTAL IMMERSION THERMOMETERS¹

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To avoid the necessity of applying the correction for the emergent stem, so-called partial immersion thermometers are made, which are pointed and calibrated to read, as nearly as possible, correct temperatures when immersed to a definite mark on the scale, *e. g.*, 8 cm. above the bottom of the bulb. The indications of such thermometers are obviously influenced to some extent by the temperature distribution above the bath; for example, if the thermometer were used in a bath, the top of which was insulated, the indications would be somewhat different from those obtained in an open bath where the emergent stem would be heated by convection currents. The difference would be still more marked if the thermometer were used in a small bath heated by a gas flame.

Such thermometers should be marked "... cm. immersion" or its equivalent, and should be provided with a mark on the stem to indicate the depth of immersion. The reliability of the corrections certified as applicable to partial immersion thermometers is necessarily somewhat less than that of the corrections certified for total immersion thermometers, but this does not by any means imply that, if both thermometers are used with partial immersion, more accurate results will necessarily be obtained with the total immersion thermometer.

RELATIVE ACCURACY OF PARTIAL AND TOTAL IMMERSION THERMOMETERS

For general laboratory use the partial immersion thermometer has some very evident advantages. In

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choosing the type to be preferred for any one kind of measurement it is necessary to decide whether the possible errors incident to the use of a partial immersion thermometer are larger than are permissible, and whether it is worth while to use a total immersion thermometer under conditions approximating total immersion or, if the total immersion thermometer must be used with a considerable portion of the stem emergent, to make an accurate determination of the stem correction. The magnitude of the possible error due to the use of a partial immersion thermometer is best illustrated by an example.

PARTIAL IMMERSION THERMOMETER AT 300°—Suppose a partial immersion thermometer to have been standardized in a certain type of bath so that, for a bath temperature of 300° C., the average temperature of the 300°-length of emergent stem was 40° and that it is later used to measure the temperature of another bath at 300°. Under the most markedly different conditions the *average* stem temperature could hardly differ by more than 50° from that which prevailed during the standardization of the thermometer. For this possible difference in mean stem temperatures in the two cases the resulting difference in the indications of the thermometer (error as used) would be:

$$0.00016 \times 300 (50) = 2.4^\circ$$

Except under very unusual conditions the error under consideration would be hardly more than half that calculated above, or, in round numbers, about 1°.

TOTAL IMMERSION THERMOMETER AT 300°—Consider next the accuracy attainable by the use of a total immersion thermometer likewise used with 300° of the mercury column emergent from the bath. If the average stem temperature is actually 40° as before, the total stem correction is

$$0.00016 \times 300 (300-40) = 12.5^\circ$$

It is at once evident that totally neglecting this stem correction, as is now the practice in many standardized commercial tests, will introduce an error many times as large as could possibly result from the use of a partial immersion thermometer. If, on the other hand, the necessary care is taken to determine accurately the large stem correction, under the above conditions of use of the total immersion thermometer, this stem correction could be determined to an accuracy of at least 0.5°, corresponding to an accuracy of about 10° in determining the average stem temperature, and in that case a somewhat higher accuracy could be attained with the use of the total immersion thermometer. If, however, the stem temperature were determined by hanging an auxiliary thermometer beside the stem, the reading of this thermometer might differ considerably more than 10° from the *average* temperature of the stem, and the resulting error in the determination of the stem correction might exceed 1°, which is comparable with the error incident to the use of a partial immersion thermometer. Obviously, if the auxiliary thermometer were hung with its bulb a short distance above the bath, it would indicate a temperature considerably in excess of the average temperature of the stem, and if placed with its bulb too

near the top of the emergent column, it would indicate too low a temperature. To determine the average stem temperature accurately, it is necessary to use a suitable capillary ("faden") thermometer, which is a thermometer with a long capillary bulb, and which serves to measure the average temperature of the portion of the stem beside it. This is a very special device that is very rarely used outside of a thermometer standardizing laboratory.

ACCURACY AT LOWER TEMPERATURES—In the above illustration a bath temperature of 300° was assumed. At lower temperatures the case is slightly less favorable to the partial immersion thermometer, because of the fact that a large part of the possible error in its use is due to differences in the temperature of the laboratory at different seasons. As an example, suppose a partial immersion thermometer is used to measure the temperature of a bath at 90°, with 90° of the column emergent; a difference of stem temperature of 30° under different circumstances is possible, corresponding to a difference in reading of 0.4°, but except under unusual conditions the difference should not exceed 0.2°. For a total immersion thermometer, with 90° emergent and an average stem temperature of 25°, the stem correction would be about 0.9°. If, as seems reasonable, the average stem temperature could easily be determined within 5° or 10°, the stem correction would be determined to about 0.1°, so that in this case somewhat more accurate results could be obtained with the total immersion thermometer, even if the stem correction were merely determined in the usual manner.

GRADUATION INTERVALS

The above considerations apply primarily to thermometers graduated in 1° or 2° intervals. For thermometers which are graduated in smaller intervals, and particularly for thermometers graduated in 0.1° or 0.2°, in the use of which an accuracy of a few hundredths of a degree is desired, the situation is not the same, as may be shown by an example.

Suppose a temperature of 70° C. is to be measured with a thermometer graduated from 0° to 100° in 0.2°. If a total immersion thermometer with 70° of the mercury column emergent from the bath is used, it may reasonably be supposed that the average temperature of the emergent stem can be determined with an error not exceeding 5° by the use of an ordinary auxiliary thermometer, or within 1° by the use of a capillary thermometer. The error in the computed stem correction, due to an error of 5° in the average temperature of the stem, is

$$0.00016 \times 70 (5) = 0.06^\circ$$

A partial immersion thermometer may be used at one time in a room at 15° C. and at another time in a room at 35° C. (usual range at the Bureau of Standards). If the same temperature (70°) were measured with the partial immersion thermometer under the two extreme conditions, the results obtained would differ by

$$0.00016 \times 70 (20) = 0.22^\circ,$$

or more than one whole scale division. The compar-

ison is less favorable to the partial immersion thermometer at temperatures lower and more favorable at temperatures higher than the one considered.

From the above considerations it will be seen that increased accuracy in the use of partial immersion thermometers cannot be had by using finer graduation intervals, such as 0.1° or 0.2° , nor can it be had by the use of total immersion thermometers graduated into such intervals, when a total immersion thermometer is actually used with a long emergent column, unless the average stem temperature is accurately determined. It seems, therefore, inadvisable to resort to such fine graduation intervals in all cases where the thermometer must be used with a long emergent column. Finely divided thermometers are presumably intended to yield accurate temperature measurements, and hence such thermometers should, in general, always be graduated as total immersion thermometers, and should be used, as nearly as possible, under conditions of total immersion; or, if that is not possible, the average stem temperature should be determined with the required accuracy. Otherwise, the increased accuracy which one would naturally expect is not attainable. The only excuse for resorting to such fine graduations in the case of a thermometer that has to be used with a long emergent column is the somewhat greater ease of reading by an inexperienced observer. It is very easy with a little practice to train anyone with moderate intelligence to estimate 0.1 of a graduation interval, so that there is no very strong reason for graduating thermometers to be used with a long emergent column finer than 1° , although, of course, this is admittedly a matter of personal preference, and depends somewhat upon how entirely untrustworthy are those to whom the reading of thermometers is entrusted. It has always seemed to the writers that laboratory assistants who could be relied upon to carry out most standardized chemical tests could equally well be expected to possess sufficient intelligence to learn quickly how to estimate thermometer readings to 0.1 of the smallest graduation interval.

The custom of some manufacturers of marking certain thermometers for "bulb immersion" is open to serious objection, first, because the term is indefinite, and, second, because the top of the bulb must be at a sufficient distance below the surface of the bath so that the entire bulb shall be at the bath temperature, as otherwise very erratic results would be obtained. The *minimum* immersion of a partial immersion thermometer in a liquid bath should be 0.5 in. (13 mm.) above the top of the bulb, and the intended depth of immersion should be marked on the stem as already noted.

Thermometers of the industrial type are very generally graduated and used as partial immersion thermometers. Where the requirements of their use are such that the thermometer is very long and the graduated part of the scale is at a considerable distance from the bulb, the two parts may be joined by thermometer tubing having a much finer capillary bore than is used in the upper portion of the stem where

the mercury must be easily seen and read. This construction minimizes the effect of temperature variations of the stem on the indications of the thermometer.

TOLERANCES AND ACCURACY OF PARTIAL IMMERSION THERMOMETERS—It will be noted that somewhat larger tolerances must be allowed for partial immersion than for total immersion thermometers, and also that the certified corrections, resulting from an ordinary routine test, are reliable to a lower order of accuracy. This is due to the fact that for total immersion thermometers the temperature of the mercury column is completely specified, while for partial immersion thermometers the stem temperature is, in the nature of the case, incompletely specified, as illustrated in the examples given above. However, if a high-temperature partial immersion thermometer were used under the exact conditions prevailing during its standardization (including room temperature) the reliability of the measurements would not be much less than of those for a total immersion thermometer actually used under conditions of total immersion.

Attention should be called to the fact that standardized methods and apparatus are used in most routine tests, and that the accuracy with which the testing laboratory can duplicate its corrections for a partial immersion thermometer is in excess of the accuracy to which the users can determine actual temperatures, where the conditions prevailing in the use of the instrument are very different from those prevailing in the test. The error due to this difference could, of course, be made very small if, for the standardized test in question, a determination were made of the correction necessary to take into account the difference in conditions prevailing during the standardization of the thermometer and during its subsequent use in the standard test.

Another procedure which might possibly receive the consideration of committees preparing standardized testing specifications is the continuance of the use of total immersion thermometers and the determination, for each such test, of the appropriate stem correction that should be applied to the reading of the thermometer at various temperatures. Such a stem correction could be determined once for all, so that it could be applied directly by the user, just as he applies the ordinary corrections taken from a certificate, provided, of course, the apparatus, including the thermometer, were standardized as to its dimensions. Obviously, the same stem correction would not apply if the thermometers differed much in their dimensions or if they were used under markedly different conditions of immersion. This procedure would take care of standardized tests, yielding results of substantially the same accuracy as would be obtained with partial immersion thermometers, but the fact would still remain that in the ordinary everyday use of thermometers in the laboratory, where stem corrections are almost always neglected, the user would, in general, get a higher accuracy by the use of partial immersion thermometers.

In considering the preparation of standard specifications for chemical thermometers for general laboratory uses, the question has arisen whether such ther-

ometers should be graduated as total or partial immersion thermometers. For the ordinary everyday use of a thermometer it seems to be quite customary to immerse it a few inches in the bath or medium, the temperature of which is to be measured. It also seems to be quite customary to neglect the stem correction. If these are the usual conditions of use it will be seen that more accurate results would be obtained by using partial immersion thermometers, and about as accurate results would be obtained by such usage as would be obtained with total immersion thermometers, even when the stem correction was applied, unless *due care* were taken to determine the stem correction with *sufficient* accuracy.

CONCLUSIONS

The above considerations may be summarized in the statement that in all cases where the application of stem corrections is neglected, which includes a vast majority of ordinary routine laboratory temperature measurements, more accurate temperature measurements would be attained by the use of thermometers graduated as partial immersion thermometers; the same statement would apply for measurements at the higher temperatures (above 200° C. or thereabouts), even if stem corrections are applied, when the ordinary method of estimating average stem temperature is used instead of the more accurate capillary thermometer method. At the lower temperatures, on the other hand, a slight advantage rests with the total immersion thermometer, if the stem correction is determined and applied in the usual manner, *i. e.*, by the intelligent use of an auxiliary thermometer to determine the average stem temperature. Thermometers graduated in intervals smaller than 0.5° C. should not, in general, be graduated as partial immersion thermometers, if the accuracy of which they are capable is desired, unless such finer graduation be deemed of sufficient importance solely from the standpoint of convenience in reading.

The Albany Chemical Company has been ordered by Federal Judge Dietrich to withdraw all applications for a trade-mark of the word "aspirin." The Company was cited by the Federal Trade Commission in complaint of unfair competition, being charged with falsely advertising that no other person or corporation has a right to the use of the word "aspirin." Upon expiration of the patent on the word, it became a descriptive name and not the property of anyone.

The *Journal of Commerce* reports that by the amalgamation of Aniline Dyes & Chemicals, Inc., with the Swiss Society for Chemical Industry, an amalgamation of the three Swiss firms, the Geigy Co., Ltd., The Chemical Works (formerly Sandoz), and the Society for Chemical Industry, with the two American firms of Ault & Wiborg and Aniline Dyes & Chemicals, is accomplished, since the recent sale of Ault & Wiborg to the Geigy Company was really a sale to the Swiss amalgamation.

A car containing 49,494 lbs. of sodium peroxide manufactured by the Niagara Electro-Chemical Company, at Niagara Falls, N. Y., recently exploded while standing on the tracks in the freight yard. No reason for the disaster has been announced.

LABORATORY THERMOMETERS

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In the following discussion "thermometer" means the usual mercury-in-glass thermometer with engraved stem. The type with enclosed glass scale is much superior for many operations, but in the ranges regularly used is not yet produced sufficiently generally in the United States to make possible its adoption as stock apparatus.

The mercury thermometer at its best is not an instrument of extreme precision. At its worst it may be very misleading. The large errors which are occasionally found are due to carelessness in manufacture, usually in the process of pointing. Excessive depression of the zero point after heating to a high temperature does not occur unless the maker has failed to use proper glass for the bulb. Irregularities in the bore rarely have any serious effect on the accuracy if the distances between reference points are not too great. If reasonable care in annealing or aging has been exercised the readings do not change much with time. Slight errors due to all these causes will be found in any thermometer and cannot be allowed for with great precision. On the other hand, a well-made, carefully pointed thermometer is as accurate and reliable as many of the other features of regular chemical work in which it is used.

The discussion by Waidner and Mueller in the preceding article covers the question of the accuracy of thermometers made to be used with total immersion or partial immersion. It is well known that a large proportion of the temperature measurements in regular chemical laboratory work are made with a greater or less length of emergent mercury column without correction.

It has been objected that errors may result from introduction of partial immersion thermometers into laboratories where those pointed for total immersion have been in use. It does not seem likely that anyone careful enough to correct for the emergent stem on a total immersion thermometer would fail to use properly one marked for partial immersion. The others would all gain in accuracy.

The specifications given below were prepared by Mr. E. F. Mueller of the Bureau of Standards to include certain features which had been suggested by various members of the Committee on Guaranteed Reagents and Standard Apparatus, and had been discussed at a conference of members of the committee with Dr. Waidner and Mr. Mueller. It was felt that the three thermometers described furnish a good working set for general laboratory use.

The thermometer with a range from —20° to 150° C. in single degrees is much more useful than one with the widely used range from —10° or —5° to 100° or 110° C., and the cost need not be much greater. The length of the degree divisions is better than on a 0° to 100° thermometer of the same length for subdivi-

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