Lewis and Storch[6] determined the potential of the bromine electrode. From this value Lewis and Randall[5] obtain the free energy of formation of bromide ion, namely

$$2E^- + Br_2(l) = 2Br^-;\ \Delta F_{298} = -49{,}190 \text{ cal.} \quad (2)$$

Gerke and Geddes[7] have found the potential of the electrode, Hg(1), Hg_2Br_2(s), Br^-, to be −0.1369 volt. From this it follows that

$$2Hg(l) + 2Br^- = Hg_2Br_2(s) + 2E^-;\ \Delta F_{298} = -NFE = -(-0.1396) \times 2 \times 23{,}074 = 6442 \text{ cal.} \quad (3)$$

The vapor pressure of a saturated ether solution of magnesium bromide at 25° has been found to be 410 mm., whence

$$2(C_2H_5)_2O(g) = 2(C_2H_5)_2O(\text{satd. soln.});\ \Delta F_{298} = 2RT \ln (410/760) = -732 \text{ cal.} \quad (4)$$

The vapor pressure of ether over a mixture of $MgBr_2 \cdot 2(C_2H_5)_2O$ and $MgBr_2 \cdot (C_2H_5)_2O$ at 25° is 390 mm. Therefore

$$MgBr_2 \cdot 2(C_2H_5)_2O(s) = MgBr_2 \cdot (C_2H_5)_2O(s) + (C_2H_5)_2O(g);\ \Delta F_{298} = RT \ln (760/390) = 395 \text{ cal.} \quad (5)$$

Likewise from the vapor pressure of ether over a mixture of $MgBr_2 \cdot (C_2H_5)_2O$ and $MgBr_2$, which is 130 mm., we obtain

$$MgBr_2 \cdot (C_2H_5)_2O(s) = MgBr_2(s) + (C_2H_5)_2O(g);\ \Delta F_{298} = RT \ln (760/130) = 1047 \text{ cal.} \quad (6)$$

If equations (1), (2), (3), (4), (5) and (6) are added and the numerical result rounded off to agree with the precision of the experimental data the free energy of formation of anhydrous magnesium bromide is obtained

$$Mg(s) + Br_2(l) = MgBr_2(s);\ \Delta_{298} = -114{,}000 \text{ cal.}$$

Summary

1. The e. m. f. of the cell, Mg(s), saturated ether solution of $MgBr_2 \cdot 2(C_2H_5)_2O$, Hg_2Br_2(s), Hg(l) at 25° has been measured.

2. The vapor pressure at 25° of the di- and mono-etherate of magnesium bromide has been determined.

3. The free energy of formation at 25° of magnesium bromide has been calculated.

LAFAYETTE, INDIANA RECEIVED JULY 31, 1933

(6) Lewis and Storch, THIS JOURNAL, **39**, 2544 (1917).

(7) Gerke and Geddes, *J. Phys. Chem.*, **31**, 886 (1927).

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

Freezing Points and Triple Points with Water

BY WALTER P. WHITE

In principle, it is easy to get a perfect freezing point for water; it needs only to mingle properly pure ice, pure water and pure air. No doubt this has often been done; rather easily for a precision of 0.002° or so. But 0.0001° has not been easy for all. One well-known worker said privately that it was impossible.[1] A very large laboratory, where thousands of ice-point determinations had been made, had come to distrust them, and was moving in the direction of triple-point apparatus. And when a carefully made ice bath of ours changed over 0.001° on slight poking, a serious investigation seemed in order.

The temperature readings were made with a thermel, which, when subjected to nearly the same temperature from end to end, is the most reliable thermometer known. Its readings are essentially differential, requiring two bodies to be read. The plan was to have, first, a triple-point bulb, as a thoroughly reliable standard temperature, and then to use this to test ice-points. Ultimately the ice-point apparatus which was developed was used to test two triple-point bulbs and show their errors.

The Ice-Point Apparatus

This apparatus, the "Cold Cell" (Fig. 1), was a logical development of an old device, namely, a cup, as of glass or metal, to protect the innermost part of the bath against external influences. Experiment soon led to a cup completely closed, with two small tubes for running water in and out without moving the ice.

With complete external protection, constancy—the chief object in our case—required the absence of any change originating within the cell. This means increase of impurity. Such may be introduced on thermometers, or may come, very slowly, through melting, absorption of air, or solution of glass or other material of the cell. Another important source, probably, is solution of specks of impurity imbedded in the surfaces

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(1) For a similar opinion, coming from the Reichsanstalt, see H. Moser, *Ann. Physik*, **1**, 341 (1929).

of the commercial ice and not dissolved out by the earlier washing. There seems to be no doubt that these impurities, since they lower the melting point, will keep going into solution as long as they are exposed. The same will happen, though much more slowly, to impurity in solid solution. If melting from other causes, which might expose new specks or regions of impurity, is prevented, the final result will evidently be that the ice will become superficially as pure as the water it is washed with, so that this water alone will determine the temperature. How long this purification of the ice surface takes and how complete it becomes are probably uncertain. Our results indicated that after a few hours at most this impurity became less noticeable than some of the other effects. Our ice, melted, showed around 0.00003 conductivity, corresponding to perhaps 0.001° lowering. One direct test showed 0.0008° or 0.0009°.

Some of these sources of error are hard to avoid completely, some are easy to overlook. It is therefore not strange that experimenters who counted on getting their baths right at the first mixing have been sceptical as to the possibilities of zero points. Proper washing of the completed bath, however, if accompanied by an absence of melting, will produce, or repeatedly restore, a reading as accurate as the water is pure, which changes with exceeding slowness. Our experience illustrates this. First, pairs of cold cells were compared during 138 days. There were 17 fillings of each, or 34 fillings in all, which were used from 1 to 17 days each. The ice, in small lumps, was washed first. Fourteen out of the 17 disagreed when first set up, 12 of them by 0.001° or more. All were, by renewing the water, brought to agreement within 0.0001°, usually within 0.00005°. One renewal of water (in each of the pairs) was enough in 8 cases, two in 5 other cases, 3 in the remaining one. In a few cases the cells were set up with some unwashed parts, yet all were brought to agreement, in others the parts were soaked beforehand in distilled water for days; but nearly all were unsatisfactory at first. After being brought to agreement the pair of cells nearly always stayed within 0.0001° of each other for from four to ten days. This was not strictly constancy; they varied together, as was easily shown by putting fresh water in one of them. This also showed the amount of change. It averaged less than 0.0001° per day. Of course the altered cells were easily and quickly brought to agreement again, and to a value which for a day or more was within 0.0001° of that corresponding to the purity of the water used.

Second, since the small drifts observed were very probably due to contamination from commercial glass or rubber, or both, a cell was made of acid-treated Pyrex glass with a sheet silver cover. This gave perfect constancy for fourteen days.

It therefore appears, both from our experiments and from logical analysis, that while it is no doubt possible, under appropriate conditions, to mix an ice-bath right the first time, it is very much easier, safer and surer to condition the bath by renewing the water. The ideal ice-point bath, so to speak, is not born but made. And this seems a complete solution of the problem which we set for ourselves.

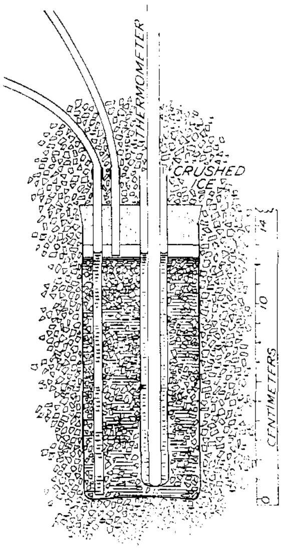

Fig. 1.—"Cold Cell" ice-point apparatus, protecting against external disturbances, having tubes for washing and replenishing with pure water.

A great advantage of the practice of renewing water in the cold cell is that it affords a means of verification, by renewing until constant temperature is reached. The cold cell also gives a ready indication of the air-saturation of the water. This comes by running water out of the cell, the first effect of which is to air-saturate completely a sample of water (that wetting the lumps of ice), which is otherwise for a while quite the same as that with which the cell was previously filled.

The only essentials of our cold cell are the covered cup and a tube for running water in and out, but other features may sometimes be desirable, especially the air tube. This gives a convenient means of telling when the cell has been filled. With the rubber stopper it can give assurance that only purified air is drawn in when water is run out. The slight impurity which the stopper probably communicates evidently does not prevent, though it complicates, the most accurate work. A paraffin cap was more satisfactory mechanically than sheet silver. Its effect on the purity of the water was not tested, but it seems promising in this respect. The carbon dioxide in ordinary air will probably not get through the outer ice in detrimental quantities, though we have not proved this conclusively.

One advantage of a triple-point bulb is that the thermometers inserted do not touch the pure water. This advantage is even more readily attainable with a cold cell. A tube, closed at the bottom and filled with water, runs down into the cell, and the (chilled) thermometer is inserted in this. This also avoids fitting different thermometers to the cover of the cell, and is easier on delicate resistance thermometers.

After several methods had been tried, fully air-saturated water was prepared by keeping a liter Pyrex flask three-quarters full of distilled water packed in ice for a few days, with occasional sucking in of fresh air freed from carbon dioxide. A few hours should suffice with continuous slow stirring. Complete air-saturation, however, is usually not really necessary, since the saturation is so easily tested. The thoroughly chilled water from this flask was forced into the cell through a rubber tube of 2.5 mm. bore which ran a few centimeters horizontally through a temporary trough filled with broken ice. A very slight warming of the water as it is run in evidently does no harm. The operation is so infrequent that the resulting melting of ice is inappreciable, nor will there be appreciable loss of air from the water saturated at zero. This rubber tube, normally used to run water in just after it had been rinsed by running the previous water out, almost certainly caused no appreciable contamination.

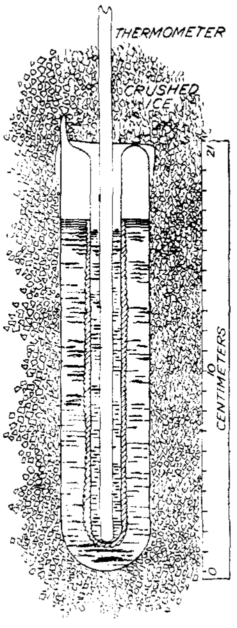

Fig. 2.—Triple-point bulb.

It may perhaps be asked: Since all it is really proposed to do to the ice is to wash it, would it not be sufficient, and simpler, merely to wash the ice with stirring, allowing enough time to purify the surface, then put it in the chilled cup and add the chilled pure water? The answer is: given pure water, proper washing and absence of melting seem necessary and sufficient for a perfect ice-point. In our case these never failed to give satisfactory results; a mere single careful filling usually failed. Our washing methods therefore seem especially reliable and worthy to be recommended. Skilful experimenters can doubtless succeed in other ways. In any case, renewing water is easier than making a cell up afresh.

Triple-Point Bulbs[2]

The triple-point method of securing a standard temperature near zero has been taken up because ice-points were not considered reliable. This supposition has just been shown to be erroneous. A sealed triple-point bulb, like Fig. 2, however, may offer the advantage of very pure water always ready. Our results indicate strongly that the ice-point is considerably easier to work with, and less liable to tricky errors, so that for work day after day it is usually much better. Normally it requires inspection or manipulation only once in two or three weeks, against two or three days with the triple-point bulb. For occasional use the triple-point method, obviating the delay and trouble of preparing air-saturated water, will be very often preferred, especially for the utmost refinement, where redistillation might also be desired for the ice-point. On the other hand, the preparation of a triple-point bulb excelling significantly in purity ordinary good distilled water, involving as it does the removal of practically all air, is a very considerable task, which may have to be repeated now and then. For instance: two Pyrex bulbs were filled for us in two different laboratories, using special methods for removing air. Distilled water had previously been left for six months in one, and then showed a conductivity of 0.0000047, not over 0.000003 (or 0.0001° probable freezing-point lowering) more than it had when put in. This bulb was filled by sublimation,[3] with a little distillation, of already re-distilled water, the operation taking three days. Nevertheless, within ten days it showed differences of temperature according to the way it was frozen, a sure sign of impurity, which was confirmed by

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(2) A. Michels and F. Coeterier, *Proc. Amsterdam*, **30**, 1017 (1927); Moser, Ref. 1.

(3) James H. Hibben, *Bull. Bur. Standards*, **3**, 97 (1929).

the reading against a cold cell. Fifteen months later more precise determinations, both the reading against a cold cell, and the change of temperature as the concentration of impurity was varied by freezing different amounts of water in the bulb, agreed in showing impurity enough to lower the reading about 0.0004°, some three times as much as for our ordinary distilled water. The other bulb was still less pure. The amount of gas left in could be estimated, and was not important.

Whatever the reason may be why these two very careful fillings gave results inferior to simply set up cold cells, the indication is strong that while it is easy to say, and is true enough, that a triple-point bulb filled with perfectly pure water has only one source of error left, the bulb may, despite much labor, be less reliable and more troublesome than the cold cell. A good way to use the triple-point bulb is immersed in ice with the thermometer stem in contact with the ice above the bulb. The ice in air will be about 0.01° below the triple point. Experiments by three different methods and a careful calculation seem to leave no doubt that with thermometer stems of 0.002 c. g. s. conductivity and 7 mm. diameter (as with our thermels) there is then no danger from conduction of cold downward, even with a little ice floating in the inner tube. This makes mercury quite needless as a heat conductor in the inner tube. It follows that the only considerable sources of error are: (1) impurities in the water; (2) a direct connection of either ice or water from the outside ice to the inner tube, that is, a failure to have an ice–water contact surface everywhere protecting the inner tube. This latter and also the distribution of impurity (if any) depend on the freezing, which therefore constitutes practically the whole art of operating this apparatus.

A common method of freezing, recommended by Moser, is to chill the bulb to, say, $-10°$ in brine, and then produce freezing by shaking. The ice is then a light network of exceedingly thin, narrow blades which, left alone, float up or otherwise disappear in a few hours, leaving clear water below. If the bulb is immediately replaced in the brine, however, the feathery ice helps to start a layer of ice all over the outer wall. A layer on the inner tube only, frozen by solid carbon dioxide in the tube, has many advantages. The freezing process is neater and easier, the layer can be inspected, repaired and otherwise controlled much more easily. Such a layer has often been kept usable for a week. Feathery ice is troublesome, but is easily got rid of when there is only one ice layer.

When ice is frozen inside the bulb the impurity becomes more concentrated in the water, less so in the ice. The resulting differences and changes of concentration, and hence of temperature, may become rather complicated and often very uncertain. The enhanced purity of the ice can be made available by melting the inner surface of an ice layer originally frozen against the tube. The skin of purest water thus produced then governs the tube temperature, which may be perceptibly higher than before the melting, when the surface of the less pure water farther out was in control. In this way the impurity can be largely circumvented, with a very close approach to the true temperature, for a time. But diffusion ultimately brings impurity into this skin of water, making the temperature uncertain. Uncertainty may also result from unintentional partial melting, rather troublesome to avoid. A layer against the outer wall, which avoids this difficulty, is harder to observe and control. With a single layer on either wall the concentration of impurity in the single body of water, and therefore the temperature, can be estimated roughly from the amount of freezing, found by observing the total volume. But this volume is continually varying, necessitating considerable manipulation of the bulb, and it is necessary to know the total amount of impurity, and therefore to have facilities for observing it. All this reinforces the suggestion made above, that the cold cell is more convenient for continuous service, the triple point for occasional use. Without impurity these difficulties greatly diminish. The cheapest way by far with the triple point seems to be through using expensive insoluble silica glass.

Summary

An ice-point at atmospheric pressure, constant to 0.0001° for a day at least, can be made with good commercial ice by protecting well the bath proper against melting from every external source and by washing the completed bath with water thoroughly chilled to prevent it from causing any general melting. With this treatment the impurities in the ice are completely removed from the surfaces, where alone they can have any effect on the temperature, and the absolute accuracy of the bath depends solely on the purity of the water. By repeating the washing occasionally the constancy can be maintained almost indefinitely. Air-saturation is easily secured and still more easily tested.

With a sealed bulb giving the triple point of water as a temperature standard there should be no error from conduction down the thermometer. Impurity in the water, however, is exceedingly troublesome, since it is both concentrated and transported by the freezing, and the configuration is continually changing. A particular method of freezing gives a relief which is excellent but only temporary, and then there seems to be no way to avoid beginning preparations all over again. Hence the triple point, while convenient and reliable for a short job, is less so than the above-described "ice-point" for continuous work. If the impurity is small enough in comparison to the requirements, however, the triple-point apparatus is excellent, though it requires more attention and work than the cold cell.

WASHINGTON, D. C. RECEIVED AUGUST 2, 1933

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Dissociation Constants of Glycine at Various Temperatures

BY BENTON BROOKS OWEN

Recently[1,2,3] it was shown that the dissociation constants and activity coefficients of weak electrolytes (including ampholytes) can be obtained from measurements of the electromotive forces of cells without liquid junctions. In applying the method to glycine,[2] the activity coefficient calculations were complete, but it was pointed out that the dissociation constants were "apparent" because insufficient data were at hand to correct for the medium effect of the glycine ions. The true (thermodynamic) dissociation constants have been evaluated in the present paper.

Discussion of the Methods

The acid dissociation constant was determined by the method of Harned and Owen,[2] making use of cells of the type

$$H_2/Z^{\pm}(m_1),\ HZCl(m_2)/AgCl,\ Ag \qquad (A)$$

Neutral glycine is represented by $Z^{\pm}$, and glycine hydrochloride by HZCl. Two stock solutions were prepared with slightly different values of the ratio, m_1/m_2, and these, in various dilutions, constitute Series A1 and A2 for which the data are given in Table I. The "apparent" hydrogen ion concentrations, m'_{H^+}, were calculated by the equation

$$E/k - E^\circ/k + 2 \log \overset{\circ}{\gamma}_{HCl} + \log m_2 = -\log m'_{H^+} \quad [20']^4 \qquad (1)$$

in which $k = RT2.3026/F$, and $\overset{\circ}{\gamma}_{HCl}$ is the activity coefficient of hydrochloric acid in pure water solution at the concentration m_2. Values of $\overset{\circ}{\gamma}_{HCl}$ were read from plots of the data of Harned and Ehlers,[5] and E° was calculated from Equation (7) of the same paper.

Representing the acid dissociation of glycine by $ZH^+ = Z^{\pm} + H^+$, and the true and apparent dissociation constants, respectively, by

$$K_A = k'_A \gamma'_{Z^{\pm}} \gamma'_{H^+}/\gamma'_{ZH^+} \quad [6'] \qquad (2)$$

and

$$k_A = m'_{Z^{\pm}} m'_{H^+}/m'_{ZH^+} = (m_1 + m'_{H^+})m'_{H^+}/(m_2 - m'_{H^+}) \qquad (3)$$

it follows that K_A is obtained by extrapolation to $\mu = 0$ on a plot of $\log k'_A$ against μ. The necessary data are given in Table I. The extrapolation is illustrated in Fig. 1, and the values of $\log K_A$ are collected in Table II.

The basic dissociation constant was determined by the method of Harned and Ehlers,[3] making use of cells of the type

$$H_2/Z^{\pm}(m_1),\ NaG(m_2),\ NaCl(m_3)/AgCl,\ Ag \qquad (B)$$

in which NaG represents sodium glycinate. The electromotive force of this cell is expressed by

$$E/k - E^\circ/k = -\log m_{H^+} m_{Cl^-} \gamma_{H^+} \gamma_{Cl^-} \qquad (4)$$

Representing the basic dissociation of glycine by $G^- + H_2O = Z^{\pm} + OH^-$, and the true dissociation constant by

$$K_B = \frac{m_{Z^{\pm}} m_{OH^-} \gamma_{Z^{\pm}} \gamma_{OH^-}}{m_{G^-} \gamma_{G^-} a_w} \quad [7] \qquad (5)$$

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(1) Harned and Owen, THIS JOURNAL, **52**, 5079 (1930).

(2) Harned and Owen, *ibid.*, **52**, 5091 (1930).

(3) Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

(4) Numbers enclosed in brackets refer to the corresponding Equation numbers in Ref. 2.

(5) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).