correlated either with the increase in molecular weight and complexity of the molecule, or with increase in the absolute viscosity. That the error is probably related to the magnitude of the molecular weight rather than the viscosity is indicated by inspection of the results with ethyl, *n*-propyl, and the hexadecyl alcohols. The data on ethyl alcohol below 0°, and *n*-propyl alcohol below 22° cover viscosities similar in range and magnitude to those of the hexadecyl alcohols between 20 and 100°. The errors in the application of equation 4a to these data on ethyl and *n*-propyl alcohols show no general regularity, whereas the errors with the hexadecyl alcohols show a pronounced curvature in the plot of log viscosity against reciprocal temperature.

Application of equations 2, 3, and 4a to materials of much greater molecular weight, such as petroleum oils, is wholly unsatisfactory except over short ranges of temperature.

Summary

1. The kinematic viscosity–temperature equation, $\log_{10} \eta/d = A/T - B$, has been fitted to the data on forty-seven organic liquids with errors in most cases of less then 1%. The constants A and B and the errors at various temperatures for each compound are reported.

2. This equation appears to be at least as accurate as the equation of Andrade[4] and is more convenient to use.

3. The error increases with increase in molecular weight rather than with increase in viscosity.

4. The equation is not suited for materials of high molecular weight such as petroleum oils.

NEW HAVEN, CONN. RECEIVED APRIL 28, 1937

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

Mixing Device for Thermochemical Calorimeters[1]

BY WALTER P. WHITE AND H. S. ROBERTS

In thermochemistry, as precision has increased, it has become more and more common to have material which is to be added to the calorimeter liquid immersed in that liquid (but not touching it) before the beginning of the calorimetric observations, the container of the material being opened at the proper time. This ensures that the temperature of the material shall be most accurately equal to that of the calorimeter, and that every bit of it shall be added to the solution. Where the added material is liquid, cells closed by rubber stoppers and similar arrangements in great variety have been used. Fairhall and Lamb (unpublished paper) used a glass cell to which was cemented by paraffin a thin glass cover which was smashed by a glass rod. When the material was powder, thin-walled glass bulbs have been used, and Frederick Barry[2] showed ingenuity and skill in making the bulbs so that when broken they should fly to pieces, leaving no cups to hold small masses of powder out of the circulating liquid.

In our case the liquid was hydrofluoric acid, so glass was out of the question. The chemical conditions made it imperative to pour the loose powder very quickly into the liquid and to do this well below the surface.

This was accomplished by means of a Redmanol[3] boat with a deck of sheet material sealed on with wax. To liberate the powder the deck was rolled up by pulling a platinum wire attached to its far end. The boat was vertical in the calorimeter, and the pull was upward against the calorimeter cover. The cover can be braced by a rod, as of hard rubber, which may be removed if desired, immediately after the pull. In our case the cover was clamped to the calorimeter whose weight, 1.5 kg., was enough to withstand the necessary pull. In placing the boat the wire must of course be thrust up through the cover. Since several successive charges of material were used on one calorimeter filling, a small lid was used over a hole in the cover, through which the boat was inserted. The wire was easily pushed through this before it was put on the calorimeter. The wire, with the wax seal, can support the weight of the boat before the pull, but it was thought best to do everything possible toward freeing the wax from mechanical strain, hence each boat was screwed to its own lid, which held it firmly in exact position and made it easy to handle.

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[1] Original manuscript received March 9, 1936.

[2] Frederick Barry, THIS JOURNAL, **44**, 1917 (1922).

[3] Probably practically the same as Bakelite.

These lids were inverted cups resting in an annular oil seal. It is they which were held down by means of the clamp on the body of the calorimeter. The inner surfaces of the boat in position were either vertical or steeply inclined, to get the powder out quickly.

One advantage of this mixing method over some others is that the final operation required one pull on a cord and nothing more. The observer near his galvanometer (if electric thermometers are used) can start the reaction without even taking his eye from the telescope.

The only critical feature of the method was making the wax hold tight, which presented a rather inexplicable amount of difficulty. The trouble was largely overcome after a stronger wax was adopted, more of it was used than at first seemed needed to cover the joint, and the surface of the deck was cleaned with especial care before any wax was put on it. There is no evidence that this last feature was important. In spite of all improvement it seemed highly desirable that each inclosure should be tested for tightness before being inserted in the calorimeter. Hence the deck was made of transparent material, a little test paper was put in with the powder, and the sealed boat was immersed for some time in hydrochloric acid and watched. No doubt after a little experience using this test it can safely be omitted, but the use of it does no harm whatever, except a little delay which at times might be undesirable.

The transparent material was nitrocellulose, 0.19 mm. thick, from old photographic films. Adopted first on account of its transparency, it proved far superior in almost every respect to the thin sheet gold that was used at first. The metal repeatedly tore, perpetually developed wrinkles, and was hard to keep flat; the cellulose nitrate was amply strong, flexible, and hardly became permanently bent at all. It was very easy, though not necessary, to cut a new one each time. The nitrocellulose became frilled if overheated, but after a little experience this ceased to give any trouble. Its lower thermal conductivity was valuable. Its resistance to the diffusion of acid through it was a surprise. An area of 4 sq. cm. passed less than 1 mg. of hydrochloric acid in forty days out of concentrated solution. Alkali was not tried. Strong caustic attacked the Redmanol seriously.

In order to facilitate pulling up the deck it was narrowed at the lower end, the bow of the boat. To do the pulling, a T of platinum wire was thrust up through a very small hole in the end of the deck, its short cross-bar against the lower side of the deck. This cross-bar was accommodated in a small pocket in the Redmanol. The stem of the T then came through a Redmanol block 1 cm. high, rounded on the lower edge away from the T to serve as a fulcrum. A pull on the wire parallel to the length of the boat then, with considerable leverage, pulled the deck

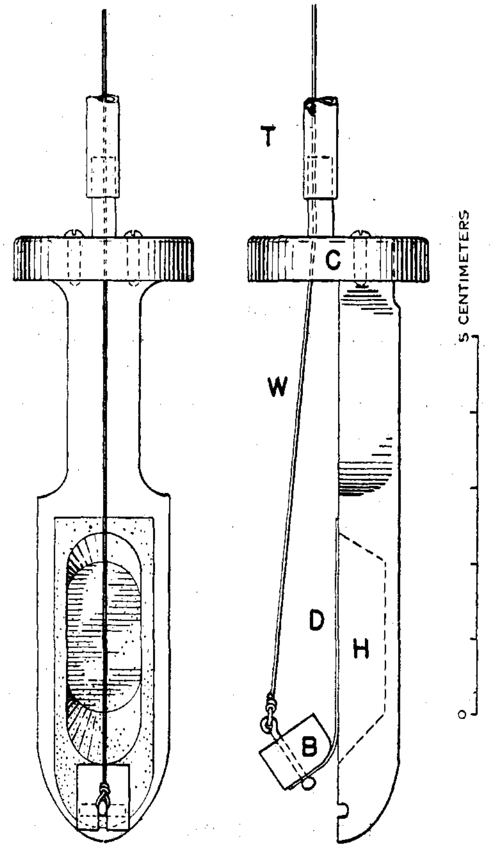

Fig. 1.—Submersible boat, deck view, and side view showing method of rolling up the deck to open. D, deck; W, wire to pull it up; B, block to transform the pull initially into a lift away from the boat; H, hold, or cavity for the powder; C, inverted cup, part of the seal on the calorimeter cover; T, narrow tube to transmit the wire while checking evaporation. The wax around and over the edge of the deck is not shown. Such a tube, even in the absence of the boat, is often valuable where oil seals against evaporation are used around the stirrer shaft or elsewhere. It transmits practically no evaporation, yet prevents spreading of the oil by bubbling of air through the seal. The width of the boat was governed by the hole, 2 cm. in diameter, already made in the calorimeter cover.

end directly away from the boat. Once started, the deck was easily rolled up.

The technique of sealing the deck in place was as follows. The boat was at first held fairly firm between two pins on a wooden bar clamped to the table. The deck, already waxed on top around the edge, was laid in place, then a brass plate was clamped down upon it. This plate was narrower than the deck, but wider than the opening in the boat. It ensured two things, first, that any part of the deck, once waxed, would not be loosened by warmth due to the waxing of an adjacent portion, and, second, that the deck just around the hole in the boat would remain cool, preventing wax from flowing in under against the powder. The waxing was done with a small nail warmed over a Bunsen burner. The wax sometimes adhered to the brass plate and might be loosened when this was raised. The easiest way to deal with this difficulty was apparently to wrap aluminum foil (0.01 mm. thick, from chocolate packages) around the plate, which could then be lifted free after the waxing. The aluminum could next be peeled off without loosening the wax. Wax was run across under the deck near the bow, so that none was needed near the wire. Premature wiggling of the wire, unless excessive, would then not endanger the seal.

The best wax, mechanically, of those we tried was picein. Picein, however, like many waxes, shows below 30° a variation in apparent specific heat, due no doubt to incipient melting. This causes the practical heat capacity of the calorimeter to vary with temperature by an amount depending on how much wax was used. With picein, however, the variation from 22 to 30° is 0.1 cal. per gram[4] per degree. Not over 200 mg. was needed, so the variation was actually 0.02 cal. per degree or 25 parts per million of the total capacity of 800 cal. per degree. Several times as much as that would ordinarily be safely negligible.

Summary

A thermochemical calorimetric mixing device will liberate powders into a solution very rapidly after they have been immersed so as to reach the calorimeter temperature. The method of opening is particularly convenient. The tightness of each seal against any sort of leakage of acid can be thoroughly tested with ease. Made for use in hydrofluoric acid, the apparatus is made of Bakelite, nitrocellulose film, and the very adherent wax, picein.

[4] The corresponding variation with some solid paraffins, due probably mostly to crystal inversions, is 7 times as great. Such waxes, in any quantity, would not be safe. More complete values on a number of waxes will be published later.

WASHINGTON, D. C. RECEIVED MAY 8, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Saturated Standard Cells with Small Temperature Coefficients. II

BY W. C. VOSBURGH, MARY GUAGENTY AND WILLIAM J. CLAYTON

It has been shown by Vosburgh[1] that adding sufficient lead or tin to the amalgam of a saturated Weston cell makes a cell that is as reproducible as the Weston cell, but has a smaller temperature coefficient. The electromotive force and temperature coefficient of the Weston cell can be altered by additions to the cadmium sulfate solution also, and it is the purpose of this paper to show the effect of adding sodium sulfate.

When another component is added to the electrolyte, another phase must be added also if a change in the variability of the system is to be prevented. Accordingly, the saturated cadmium sulfate solution of the Weston cell was replaced by a solution saturated with both cadmium sulfate, $3CdSO_4 \cdot 8H_2O$, and the double salt of sodium and cadmium sulfates, $CdSO_4 \cdot Na_2SO_4 \cdot 2H_2O$.[2] The result was a cell with an electromotive force of 1.01668 v. at 25° and a temperature coefficient about 10% higher than that of the Weston cell. By replacing the cadmium amalgam of this cell with a cadmium-bismuth amalgam[1] (p. 2537) a cell was obtained having an electromotive force of 1.0184 v. at 25° and a positive temperature coefficient between one-quarter and one-third of that of the saturated Weston cell.

Materials.[3]—Mercury was purified by distillation in a current of air. One preparation of mercurous sulfate was made by precipitation from mercurous nitrate and sulfuric

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[1] Vosburgh, THIS JOURNAL, **47**, 2531 (1925).

[2] A solution saturated with sodium sulfate and the double salt might also be used, but this system has a transition point at 31° according to "International Critical Tables," Vol. IV, p. 340.

[3] For the preparation of some of the materials the authors are indebted to Mr. Gerald R. Cooper and Miss Barbara Pettengill.