atmospheres, under conditions where the possible passage of mercury must be provided for. These joints were tested to 50 atmospheres before use.

Acknowledgments are due to H. F. Stimson and C. H. Meyers, of this Bureau, for assistance and suggestions.

7. Summary.

1. Methods for the construction of 2 types of metal to glass joints have been given together with the results of tests upon their behavior on handling, their vacuum tightness and their resistance to internal pressure.

2. A reproducible and quantitative method for making and breaking connections between metal and glass or glass and glass is given.

3. Several types of apparatus and laboratory work in which these joints can be successfully used have been outlined.

WASHINGTON, D. C.

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

A CALORIMETRIC METHOD FOR STANDARDIZING THERMOMETERS BY ELECTRICAL ENERGY.

BY THEODORE W. RICHARDS AND SETSURO TAMARU.

Received April 23, 1920.

In 1915 Dr. Thorbergur Thorvaldson, in collaboration with one of the present authors, showed that it was possible to calibrate an interval in the thermometric scale near the temperature of the room with considerable accuracy by means of a definite chemical reaction repeated step by step at intervals over the scale.[1] This method (which demands only very simple apparatus) might serve, when properly carried out, a useful purpose for those whose experimental appliances are limited. Nevertheless, the change in heat capacity, and of heat of reaction with the temperature, cause complications in the calculation; and these data demand more thorough study as to their details before the method can attain the highest accuracy of which it is capable.

Another somewhat similar method is the subject of the present paper. In this method, the source of energy is not a chemical reaction, but rather electrical energy supplied at known voltage through a definite constant resistance. The method consists simply in thus supplying heat in successive small equal quantities to a calorimeter, noting the reading of the thermometers produced by each step. From the known heat capacity of the system, the rise of temperature which ought to occur is easily calculated. The comparison of the actual rise in each case with that calculated should give the error of the thermometer over each interval concerned. The accuracy clearly depends first, upon the accuracy of meas-

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[1] Richards and Thorvaldson, THIS JOURNAL, 37, 81 (1915).

urement of the time and the several electrical dimensions; secondly, upon the precision of the calorimetry; and lastly, upon the accuracy with which the specific heat of the system (consisting largely of water) is known.

The mode of experimentation is, of course, such as might be suited to the determination of heat capacity, if the temperature intervals were known. Instead, the heat capacity of water is assumed to be known and the temperature scale thus determined. The well-known work of Barnes[1] has placed our knowledge of the specific heat of water at ordinary room temperatures in a position adequate for the present purpose.

Apparatus.—The calorimeter was adiabatic, being contained in a closed vessel submerged in a bath capable of being heated electrically at the same rate as the inner calorimeter itself. The heating coil for the inner vessel was made of seasoned manganin coated with a firm insulating film of Bakelite; its 2 stout leads were suitably insulated by glass tube and sealing wax. This coil was immersed deeply in 0.9 liter of water in the calorimeter proper. The calorimeter was separated by an air space about 5 mm. thick from the walls of the submerged container. Such an air space was found to be sufficient, a wider space effected no important gain. The stirring was accomplished by means of the up-and-down motion of a stirrer composed of 2 perforated flat, silver rings which were thermally insulated from the operating mechanism by means of vulcanized rubber, so that there was no heat exchange through this agency. The mercury thermometers to be calibrated were immersed in the inner calorimeter vessel to a definite depth, kept constant throughout the experiments.

The surrounding bath was provided with a vigorous stirrer to cause very rapid attainment of uniformity in the temperature of the bath. Suitable rheostats and electrical measuring instruments were provided for both the inner and the outer circuits. The accurate measurement made necessary in the inner heating coil was made by means of a potentiometer so arranged that the potential between the terminals of the heating coil should be kept constant within 0.02% (at a value definite in any given series and usually about 3 volts). A stop watch measured the equal intervals of time. Neither potentiometer nor heating resistance need be carefully calibrated if the object is simply to subdivide a given interval of the thermoelectric scale and absolute values are not needed. A normal cadmium cell which was sufficiently constant served as the standard of electromotive force.[2]

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[1] H. T. Barnes, *Phil. Trans.*, **199A**, 149 (1902).

[2] The arrangement was not unlike that used by F. Daniels and one of us, except that, of course, the calorimeter and heating coil were much larger in the present case (THIS JOURNAL, 41, 1746 (1919)).

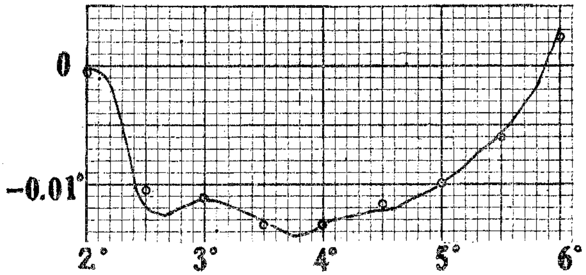
The successive readings indicated on a Fuess Beckmann thermometer (set so that 2.000° on its scale = 16.00°) through successive additions of a given amount of electrical energy in one of the series of trials are given by the following figures: 2.0505, 2.5555, 3.051, 3.5475, 4.044, 4.5375, 5.032, 5.5225 and 6.008.

The several differences between the successive pairs of these 9 figures are: 0.5050, 0.4955, 0.4965, 0.4965, 0.4935, 0.4945, 0.4905, and 0.4855.

If the specific heat of water at 18° is taken as 1.0000, those at 16° and 20° may be taken as 1.0005 and 9.9995, respectively. Evidently the corrections to be applied to the various differences on account of these small changes are very small,—beyond the accuracy of reading; but collectively they are worth considering. The values of the differences thus corrected become as follows: 0.5053, 0.4957, 0.4966, 0.4965, 0.4935, 0.4944, 0.4903 and 0.4858. The sum total of these 8 figures is 3.9581.

Careful determinations of this total interval by a standard platinum resistance thermometer showed that it was really 3.961°. Hence each interval should have been 0.4951°. The difference between this number and each of the 8 before mentioned gives the error of that particular range. Thus the error of the thermometer between 2.05 and 2.55 on its scale is found to be +0.0102°, between 2.55 and 3.05 +0.0006°, and so on. The corrections to be applied of course, bear the opposite sign.

The average of 6 trials thus made with this thermometer gave the results for its corrections indicated in the diagram, where they are compared with a careful standardization of the same thermometer by means of an accurate platinum resistance thermometer (standardized at the Bureau of Standards), kindly made by Mr. O. C. Bridgeman.



Corrections to the Beckmann thermometer are plotted in the direction of ordinates; scale readings of the thermometer in the direction of abscissas. The black line indicates standardization by platinum thermometer; the circles, the average results of the method under consideration.

The 6 trials of which the average is represented above were the last executed of a number in which the earlier trials served as preparation and training. The intervals were not always half a degree, as in the case cited, some being less and some more. Of the 60 observations included in these 6 series of results, only 2 deviated from the smooth curve drawn among them by more than 0.001°. Thus it is clear that with adequate practice and care this method may serve very satisfactorily to calibrate a thermometer.

We are indebted to the Carnegie Institution of Washington for generous pecuniary support in this work, which was incidental to a careful research having as its main object the determination of the heat of solution of cadmium in acids. This will soon be reported in full. The experimental work was completed in 1915.

Summary.

In this brief paper, it is shown that a thermometer may be accurately calibrated by successive additions, to a known heat capacity, of heat from electrical energy. The experimentation is essentially like that suitable for the determination of heat capacity where temperature changes are accurately known.

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[CONTRIBUTION FROM CHEMICAL LABORATORY, EDGEWOOD ARSENAL, EDGEWOOD.]

FREEZING-POINT SOLUBILITY CURVE FOR SULFUR AND DICHLORO-ETHYL SULFIDE.[1]

BY J. A. WILKINSON, CHRIST NEILSON AND H. M. WYLDE.

Received April 28, 1920.

In the preparation of dichloro-ethyl sulfide or mustard gas by the reaction between ethylene gas and sulfur monochloride according to the equation

$$2C_2H_4 + S_2Cl_2 = (C_2H_4Cl)_2S + S$$

one atom of sulfur is set free for every molecule of mustard gas formed, that is, about 20% of sulfur by weight. When first prepared this sulfur stays in solution, but on standing it may precipitate out in such a way as to form a hard cake in the settling tanks or pipe lines. Later methods of manufacture overcame this difficulty, however.

It was the purpose of this investigation to determine the solubility of sulfur in liquid mustard gas and also the nature of the solid phase which separates out at different temperatures.

Preparation of Materials.

The first experiments were made with a very high grade of roll sulfur without purification. Afterwards pure rhombic, monoclinic and amorphous sulfur were prepared and their solubilities determined.

Rhombic sulfur was prepared by recrystallizing the roll sulfur from carbon disulfide solution.

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[1] Published with the approval of Lt. Col. Amos A. Fries, Chief Chemical Warfare Service, U. S. A.