

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

A NEW THERMOCHEMICAL METHOD FOR SUBDIVIDING ACCURATELY A GIVEN INTERVAL ON THE THERMOMETER SCALE.

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Heretofore the scientific world has relied primarily for its exact temperature scale upon the careful study of the expansion of hydrogen made at the Bureau des Poids et des Mesures. The reduction of this hydrogen scale to the true thermodynamic scale has been the subject of much interesting discussion.¹ But for several reasons, which need not be amplified here, the outcome is not wholly satisfactory, hence new methods of fixing the standard scale are earnestly desired. The linear temperature coefficient of the electrical conductivity of platinum is being strongly advocated by some as the standard, and seems at present to possess several advantages.² Nevertheless, this is no reason for withholding other suggestions; and, accordingly, the present paper describes an entirely new method of subdividing a small interval, which relies upon a thermochemical application of the first law of thermodynamics.

We were led to this method by inconsistencies amounting sometimes to over half of 1% in accurately conducted thermochemical experiments. These were numerous, involving heats of combustion, heats of dilution, heats of neutralization, and heats of solution of metals. The cause of the trouble might have been either (a) in experimental error, (b) in the thermodynamic reasoning involved, (c) in the measurement of the heat capacities or (d) in the measurement of the temperatures; but careful study led us to reject alternatives (a), (b) and (c). Accordingly, (d), only, remained; *i. e.*, the temperature scale must be in error. The irregularities were of such a character as to seem to show that the 18°-point on our standard thermometers (which had been calibrated with considerable care in Paris) was not exactly half-way thermodynamically between the 16° and the 20° point.

Therefore, it occurred to us that phenomena capable of showing such an inconsistency could be used, working backwards, to calibrate the thermometers; and, accordingly, a very simple reaction was chosen for this purpose. The problem was simply to conduct this reaction at various temperatures, in such a way that the final temperature of one trial should be the initial temperature of the next, thus covering the whole interval to be

¹ See for example, E. Buckingham, Bureau of Standards, Reprint No. 57 (Vol. 3, 1907). Burgess, *J. Chim. Phys.*, **11**, 529 (1913).

² Jaeger and von Steinwehr, *Ann. der Phys.*, [4] **43**, 1165 (1914) and others.

studied step by step in a way analogous to the Ostwald calibrator for a buret.

The heat of dilution of hydrochloric acid was chosen, on account of its ease of measurement, its easily regulated magnitude, and the comparatively simple nature of the heat-capacity problem involved. The acid was diluted calorimetrically in an apparatus described in detail in a previous paper;¹ the device was found to give very consistent and satisfactory results. By choice of varying initial concentrations of acid and of varying final concentrations, one can obtain at will a temperature-change anywhere from a few thousandths to several tenths of a degree—exactly such ranges as are likely to be required.

In the case to be described, acid of the precise concentration $\text{HCl} \cdot 20\text{H}_2\text{O}$ (9.18% or about 2.64 normal) was diluted with exactly 80 H_2O , causing it to become about 0.57 normal. This reaction gives enough heat to raise the total amount of liquid about 0.25° , a very convenient interval to use as a sort of thermodynamic yard-stick in subdividing the interval of 4° needed in thermochemical investigations.

Sixteen successive temperature increments during the dilution of successive portions of this sort, covering the whole scale between 16° and 20° , were as follows after correction for the heat of stirring (0.0005° per experiment): 0.2505° , 0.2520° , 0.2535° , 0.2535° , 0.2550° , 0.2550° , 0.2565° , 0.2575° , 0.2585° , 0.2575° , 0.2590° , 0.2585° , 0.2600° , 0.2595° , 0.2615° , 0.2605° . All these temperatures are given in terms of a standard scale, obtained after due correction from carefully standardized thermometers of excellent manufacture. It is evident that whereas at first the rise of temperature in the reaction seemed to have a temperature-coefficient of nearly 0.004° per degree, toward the end it seemed to possess no temperature-coefficient at all. This irregular performance suggests at once that something must be wrong with the thermometric scale; and the deviations are precisely in the same direction, and of the same order of magnitude as the earlier inconsistencies which led to this work.

If the heat capacity of the reacting substances remained unchanged during the dilution, the heat of dilution would remain constant, over the whole range, according to the well-known law of Kirchhoff.² In that case, the deviations of each of the numbers just given from their average would give at once the error of each number, and therefore the correction which should be applied to the thermometric readings over each short range. But with the particular reaction in question, this is not the case; the heat capacity of the system really diminishes appreciably during the reaction, and accordingly the heat of reaction increases appreciably

¹ Richards, Rowe and Burgess, *THIS JOURNAL*, **32**, 1179 (1910).

² See, for example, Richards, *THIS JOURNAL*, **25**, 209 (1903).

as the temperature rises. This increase is to be found by actually measuring the heat capacities of the factors and products—a measurement from which errors of the thermometer may be wholly eliminated by making the determination over the same range in each case. In this way it was determined that the heat capacity of $\text{HCl} \cdot 20\text{H}_2\text{O} + 80\text{H}_2\text{O}$ is 1778.5 and that of $\text{HCl} \cdot 100\text{H}_2\text{O}$ is 1772.3 (if the heat capacity of a gram of water is unity)—a loss of 6.2 calorie units of heat capacity during the reaction.¹ This signifies that the heat of dilution increases 0.00348° per degree, or 0.00087° for the quarter-degree interval between successive trials.² The value of the temperature-increment thus found for each stage of the dilution only holds exactly, however, in the ideal case in which (a) the apparatus, used for dilution has no heat capacity; (b), the change of heat capacity has no temperature-coefficient; and also when (c), the standard of reference of heat capacity (water), is likewise unchangeable over the total range concerned. The first and the last of these conditions obviously do not hold in the present case; but, fortunately, each is a matter susceptible of experimental solution. For: (a), the heat capacity of the apparatus, is easily calculated (in our experiments it was 1.643% of the total); (b), the change of heat capacity was found by actual measurement to be very nearly independent of temperatures between 16° and 20° ;³ again (c), the specific heat of the standard (water), has been determined by Barnes with great care by means of a platinum resistance thermometer (in a way practically independent of the hydrogen thermometer) to be 1.00105 at 16° if the value at 20° is taken as unity.⁴ This latter change is slight, amounting to only 0.000016° for each stage of the dilution—a relatively small proportion of the whole. In this case it almost exactly balances correction a. Correcting for these three minor influences, the theoretical increase in the temperature of each heat of dilution is found to be 0.00087° . If now we assume, as a preliminary step, that the first dilution should have given 0.25027° ⁵ as its correct temperature rise, the successive theoretical heats of dilution will progress regularly as follows: $0.25027^\circ, 0.2511^\circ, \dots, 0.2624^\circ, 0.2633^\circ$. The difference between each of

¹ These determinations were carefully made but they cannot be considered as more than preliminary ones; the details will be recorded in another place.

² Each rise of temperature due to heat of dilution was a trifle over the quarter of a degree, but they overlapped by a few thousandths of a degree, so that the 16 intervals really covered almost exactly 4° . The slight overlapping does not introduce any perceptible error.

³ If this is later found not to hold precisely, due correction can easily be applied.

⁴ N. B.—Although there may be some doubt about the *absolute* value of the specific heat of water, the *slope* of the curve at this point is probably quite near enough the true value for our present purpose. See Barnes, *Phil. Trans. (A)*, **199**, 149 (1902).

⁵ This number was chosen by trial because it makes the correction at 20° the same as at 16° ; it assumes that this interval is indeed exactly 4.0000° .

these sixteen calculated values and the corresponding sixteen actual measurements mentioned on page 82, line 21, will give the error of the thermometer's reading over each of the short ranges, and the sum of all these partial errors down to any desired point will be the total errors to that point. In this way, the thermometric errors depicted in the following diagram were found in the special case chosen as an example, the values being plotted as ordinates, and the thermometer readings as abscissae.

Of course, since this is merely a relative matter, any one of the temperatures may be assumed as the standard of reference for these errors. As drawn, it was assumed that the correction at 17.14° was zero, in order to have about as many of the errors positive as negative; the reason of this choice will appear shortly. The shifting of the standard of reference shifts the whole curve bodily up or down, without affecting the algebraic

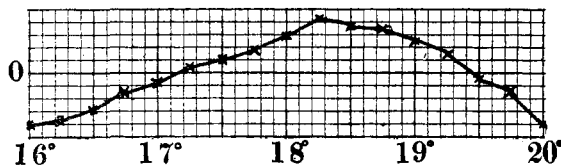


Fig. 1.—Errors of the thermometric scale in question. Scale readings are plotted as abscissas; errors (in thousandths of a degree) as ordinates.

differences of the corrections. For practical purposes it would be more convenient and less confusing to invert the curve (because a *plus* error means a *minus* correction) and to assume the lowest point of the resulting curve (18.25 in this case) as zero, so that all the corrections would be positive, and could be added directly to the thermometer reading.

A definite arbitrary change in the magnitude of the initial standard interval (in this case 0.25027) would change the general slant of the curve without altering its general character. Such a change alters the fundamental interval covering the whole range, and each part of this interval proportionately. The value 0.25027 was chosen because then the correction at 20° becomes the same as that at 16° , as already stated.

On the other hand, a change in the *increment* of the standard interval alters the character of the curve. This change is not arbitrary, but depends upon the measurements of the heat capacity, which must be executed with accuracy. It may be shown that the same actual degree of nicety is needed in this part of the work as in the work concerning the heat of

dilution, but lack of space forbids the detailed explanation. If the final curve is to have an accuracy in every part of 0.0005° , the change of heat capacity must be known to within about 0.25 calorie unit, which corresponds to an error of 0.001° over an experimental range of 4° , supposing that the calorimeter holds a liter of liquid.

It will be noted that this method does not attempt to fix the value of the standard interval with reference to the whole range $0-100^\circ$. The method gives only a means of *subdividing* any interval chosen as a standard (in this case the four degrees between 16° and 20°). To cover the whole range one would be required to carry out dilution experiments (or some other well-studied reaction) over the whole range. On the other hand, the method does provide a method for calibrating thermochemical thermometers, possessing just the degree of accuracy which is needed for thermochemical purposes.

The dilutions recorded in the special case above were verified by a similar series with a smaller rise of temperature (0.22), diluting $\text{HCl}\cdot 20\text{H}_2\text{O}$ to $\text{HCl}\cdot 121.5\text{H}_2\text{O}$. The curve in this series showed essentially the same features as the other, and need not be given in detail.

The shape of this curve given above is of more than passing interest, because it tells of corrections to be applied to the scale of a thermometer assumed to be trustworthy—the best that could be furnished a decade ago from a supposedly competent source. On the whole, it is seen to support the excellent work of the maker and of the standardizer; as recorded above, only one of the seventeen readings deviates more than 0.004° from its true value. But, nevertheless, the combined effect of these variations is a very serious matter, for the face-value of the interval between the true 16.000° and 18.000° is 2.007° , whereas between 18.000° and 20.000° is only 1.993° . In other words, there will be a discrepancy of 0.7% between the results obtained respectively over these two ranges: a very serious matter in accurate work. It was just such discrepancies which led to the undertaking of this new method; and it is pleasant to find that the new temperature scale removes many if not all of these discrepancies. But the chronicle of these details must be reserved for later communications. The question as to whether the errors are due merely to peculiarity in our standard thermometers, or are to be ascribed to the standard to which they in turn were referred, must be left to future research.

The results recorded above are only preliminary. The most difficult part of the performance (namely, the determination of the heat capacities of factors and products) can be determined once for all with great accuracy, and these figures can then be used by anyone, in any part of the world, for the computation of his results. The work required for the verification

of any thermometer will then consist simply in a series of dilutions (sixteen are obviously needed to cover 4° in 0.25° steps). This experimental work is very easily done, and with the adiabatic calorimeter is capable of great accuracy. Of course other reactions also, besides the heat of dilution of hydrochloric acid, could be used for this purpose, after they had been properly studied. Heat of neutralization of acids may be especially convenient. In case any interval appeared to be especially abnormal, it could be subdivided still further by a yet feebler reaction. We have already made further progress along these lines, and hope soon to publish a more complete account, which we hope may be really useful to chemists and physicists dealing with the difficult subject of exact thermometry.

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Summary.

A new method for subdividing accurately any given interval on the thermometer scale is presented. This method depends upon the execution of a given simple reaction step by step over the range in question, somewhat analogously to the calibration of a buret with the Ostwald calibrator. Allowance must be made, of course, for the temperature-coefficient of the reaction, and other details dependent upon changing heat-capacity. The method is peculiarly suitable for the standardizing of short ranges, such as those used in thermochemistry.

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THE SEPARATION OF TUNGSTEN FROM MOLYBDENUM.¹

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With the extensive introduction of tungsten and molybdenum into industrial chemistry in the form of the special steels and the filament of the incandescent electric lamp, the importance of these metals has been greatly increased from the standpoint of the analytical chemist.

It is a well-known fact that molybdenum always accompanies tungsten in its ores, and it shows a marked tendency to remain with the tungsten throughout the process of manufacture. This amount of molybdenum, although small, interferes to a great extent with the determination of the tungsten, and hence one of the important problems in modern analysis is to devise a separation of the two metals which will be easy to carry out and also be of the highest accuracy. Up to the present time there have

¹ From the author's Ph.D. thesis, 1914.