

corrections are included in the values of column two of Table II, in which the changes in observed microvolts are tabulated. The change in the thermocouple correction with change in temperature was also considered in calculating the temperatures, tabulated in column three of Table II. The values lie on a reasonably smooth curve, fitted by the equation

$$C_p = 2.69 + 0.0560 T - 2.66 \times 10^{-4} T^2 + 4.35 \times 10^{-7} T^3$$

The values in the last column of Table II have been calculated by the use of the above equation.

### Summary

1. The heat capacity of metallic selenium was determined by the Nernst method. The selenium was carefully purified by the Lenher and Kao method.

2. The experimental values for the temperature range from 100 to 300°A. lie between 6.08 and 7.25. Values for this range have not been reported previously. The value calculated for 300°A. is approximately ten per cent. larger than that reported by Bettendorf and Wüllner.

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### NOTES

#### The Standardization of Weights

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The method of Richards<sup>1</sup> for calibrating a set of weights has one particularly attractive feature, the procedure used in calculating the corrections from the system of observation equations. The discussion which follows will show that this procedure gives values which are exactly the same as the values defined by the system of equations. In other words, they are identical with the values to be found by substituting in algebraic formulas like those of Kohlrausch.<sup>2</sup>

**The Reasoning of Richards.**—A study of what Richards has written will explain why some do not appreciate just how accurate the calculation is. His preliminary values are *consistent* by reason of two assumptions. First, there is the assumption that the first centigram weight, called the standard of comparison, has the mass of 0.01 g. Second, it is implicitly assumed that the small differences between the masses of the various combinations of weights have been correctly measured by the rider in terms of grams. These consistent values are then translated into other terms by a method depending upon the properties of small numbers in presence

<sup>1</sup> T. W. Richards, *THIS JOURNAL*, **22**, 144 (1900); *Z. physik. Chem.*, **33**, 605 (1900).

<sup>2</sup> F. Kohlrausch, "Lehrbuch der praktischen Physik," 11th edition, p. 62.

of large ones.<sup>3</sup> This reasoning may well confuse those who study it carefully. Semon,<sup>4</sup> for example, was guided by it in making his analysis.

**A Different Interpretation.**—That procedure of Richards will now be explained in a different way. Let the symbol ( $A$ ) denote the actual number of grams in the mass of the weight whose face value is  $A$  grams. Moreover, let (0.01) denote the mass of the first centigram weight. Then, if  $[A]$  and  $[0.01]$  are the corrections for these weights, the relation between their masses is expressed by the equation

$$(A) = [A] + 100 A \{(0.01) - [0.01]\}$$

The first step in calculating the corrections is to find from the equations a preliminary value for each weight. In doing this we shall make no assumption regarding the mass of the first centigram weight. The preliminary values in Table I are *defined* by assigning to (0.01) the value 0.<sup>5</sup> Hence, it follows immediately from the preceding equation that

$$\text{Preliminary value of } (A) = [A] - 100 A [0.01]$$

TABLE I

( $A$ )	Observation equations	Grams	Preliminary values [ $A$ ] - 100 $A$ [0.01]	Aliquot parts 100 $A$ [0.01]	Corrections [ $A$ ] milligrams
(0.01)	...	.....	0.00000	+0.00007	+0.07
(0.01')	= (0.01)	-0.00006	- .00006	+ .00007	+ .01
(0.01'')	= (0.01)	- .00009	- .00009	+ .00007	- .02
(0.02)	= (0.01) + (0.01')	- .00004	- .00010	+ .00014	+ .04
(0.05)	= $\Sigma(0.05)^a$	- .00013	- .00038	+ .00035	- .03
(0.1)	= $\Sigma(0.1)$	- .00013	- .00076	+ .00070	- .06
(0.1')	= (0.1)	+ .00006	- .00070	+ .00070	.00
(0.2)	= (0.1) + (0.1')	+ .00002	- .00144	+ .00141	- .03
(0.5)	= $\Sigma(0.5)$	+ .00005	- .00348	+ .00352	+ .04
(1)	= $\Sigma(1)$	- .00008	- .00709	+ .00703	- .06
(1')	= (1)	+ .00013	- .00696	+ .00703	+ .07
(1'')	= (1)	+ .00003	- .00706	+ .00703	- .03
(2)	= (1) + (1')	+ .00002	- .01403	+ .01407	+ .04
(5)	= $\Sigma(5)$	+ .00004	- .03510	+ .03517	+ .07
(10)	= $\Sigma(10)$	- .00014	- .07038	+ .07035	- .03
(10')	= (10)	+ .00030	- .07008	+ .07035	+ .27
(20)	= (10) + (10')	+ .00043	- .14003	+ .14069	+ .86
(50)	= $\Sigma(50)$	+ .00024	- .35049	+ .35173	+1.24
(100)	= $\Sigma(100)$	- .00067	- .70189	+ .70347	+1.58

<sup>a</sup> The meaning of this notation is shown by the following example:  $\Sigma(5) = (2) + (1'') + (1') + (1)$ .

<sup>3</sup> When  $\alpha$  and  $\beta$  are quite small in comparison with  $N$ , then  $N(N + \alpha)/(N + \beta) \simeq N + \alpha - \beta$ .

<sup>4</sup> W. L. Semon, *J. Chem. Ed.*, 2, 132 (1925).

<sup>5</sup> As we are giving a definition, this value may be chosen arbitrarily. The preliminary values of Richards would result from setting (0.01) = 0.01000.

This equation easily explains the rest of the procedure. Let the last term *define* what we mean by the aliquot part for (*A*). Then it is self-evident that, when the aliquot part for one weight is known, the aliquot parts for all the others can be found. Theoretically, if we know the correction for *any* one weight, we can quickly calculate the corrections for all the others. In practical work, however, the face value of the standard should not be less than that of the largest weight in the set.

This explanation of the procedure of Richards makes no assumption and requires the use of no approximation. Consequently that procedure gives values which are precisely the same as those defined by the system of equations, and the accuracy of those values depends solely on the errors made in measuring the small differences between the masses of the various combinations of weights.

Another convenient method of arranging the computation is shown in Table II. This arrangement has the advantage of using smaller numbers. A few additional remarks will make the procedure clear. In dealing with the first group we know the mass of the weight (100) and we define the preliminary values by assigning to (10) the value 0. When we come to the second group, we know the mass of the weight (10) and we define the preliminary values by assigning to (1) the value 0.

TABLE II

Observation equations	Grams	Preliminary values	Aliquot parts	Corrections, milligrams
(10) . . . .	. . . . .	0.00000	-0.00003	-0.03
(10') = (10)	+0.00030	+ .00030	- .00003	+ .27
$\Sigma(10)$ = (10)	+ .00014	+ .00014	- .00003	+ .11
(20) = (10) + (10')	+ .00043	+ .00073	- .00007	+ .66
(50) = $\Sigma(50)$	+ .00024	+ .00141	- .00017	+1.24
(100) = $\Sigma(100)$	- .00067	+ .00191	- .00033	+1.58
(1) . . . .	. . . . .	0.00000	-0.00006	-0.06
(1') = (1)	+0.00013	+ .00013	- .00006	+ .07
(1'') = (1)	+ .00003	+ .00003	- .00006	- .03
(2) = (1) + (1')	+ .00002	+ .00015	- .00011	+ .04
(5) = $\Sigma(5)$	+ .00004	+ .00035	- .00028	+ .07
(10) = $\Sigma(10)$	- .00014	+ .00052	- .00055	- .03 <sup>a</sup>

<sup>a</sup> This value has been taken from the corrections for the preceding group of weights.

**Summary.**—The procedure of Richards for calculating corrections from the system of observation equations has been discussed. It has been shown that this procedure gives values which are identical with those to be found by substituting in algebraic formulas like those of Kohlrausch.