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Chemistry. — "*The Use of the Thermopile of* Dr. W. M. MOLL *for Absolute Measurements.*" By N. H. SIEWERTSZ VAN REESEMA. (Communicated by Prof. J. BÖESEKEN).

(Communicated in the meeting of Sept. 29, 1917).

For a number of Photochemical researches, carried out in the Phys. Chem. Lab. of the Technical University of Delft, use was made of the Thermopile and the Galvanometer of Dr. MOLL.

In order to be able to express the measured light absorptions in an absolute measure, it proved necessary to gauge the thermopile. What follows here is a preliminary communication about the measurements referring to this, the particulars of which will be published in my Thesis for the Doctorate.

The idea to gauge the thermopile by means of a Hefner-lamp or another normal lamp or also by an incandescent lamp tested e.g. by the "Physikalisch Technische Reichsanstalt" was relinquished. A direct method was preferred, (without use being made of auxiliary light sources, Hefner-lamp or other normal lamp), which could be carried out by the investigator himself in a simple way, independent of the measurements of others made in other laboratories.

Besides it would be possible, as will appear, to avoid the measurement of illuminated surfaces (here therefore a thin line of light on the thermopile) and the measurement of the distance from illuminated surface to light source, which becomes necessary in the use of a normal lamp in the indirect method.

At first it was my intention to make use of the compensation Pyrheliometer of ANGSTRÖM or of a simplified application of the principle on which it is based.

The course of procedure would have been as follows. A quantity of light in the form of a thin streak of light is made to fall on the platinum plate of the Pyrheliometer, and the electrical equivalent by compensation is measured. An electric current is namely conducted through another plate of the same shape. Behind the plates there are found thermo-elements, which have been adjusted in such a way that their electric forces work in opposite directions. Thermo-elements and plates are of the same shape. If the quantity of absorbed light in one plate is equal to the quantity of heat generated by the electric current in the other plate, the two E.M.F. must neutralize each other, and then we may write: $I = i^2 r$, in which I represents the quantity of light absorbed per time unit, i the electric current, r the electric resistance in the plate. When I has been measured in this way, the pyrheliometer is removed and the thermopile is put in its place.

If U_I is the deviation that the galvanometer gets in consequence of this, then:

$$kU_I = I = i^2 r, \text{ hence } k = \frac{i^2 r}{U_I},$$

k is a constant. In this way the pile and the galvanometer are gauged, k indicates the quantity of energy falling on the thermopile, which causes the unity of deviation.

In a conversation on this subject Dr. Moll suggested a great simplification in December 1915. Instead of the pyrheliometer a blackened platinum plate might be placed immediately before the pile. Then no special apparatus is required for the gauging, but a plate is simply slid before the pile, which plate is subsequently illuminated, then an electric current is passed through it, while the corresponding deviations in the galvanometer are measured.

Dr. Moll was so kind as to give me a quantity of Wollaston plate, for which I express my indebtedness to him here, and through which he enabled me to work out and apply his excellent idea.

The mode of procedure was now as follows:

A plate was slid before the pile, an electric current was conducted through it.

Let us then call the deviation in the galvanometer belonging to the thermopile, U_i.

The strength of the current led through the plate, i.

Its resistance r.

We then write:

$$U_i k' = i^2 r \quad \ldots\ldots\ldots\ldots \quad (1)$$

Then a beam of light originating from some constant source of light or other, for which in my case a Nernst-lamp served, was thrown on the plate.

Let us call the deviation of the galvanometer U'_I and put the quantity of light $= I$, then:

$$U'_I k' = I \quad \ldots\ldots\ldots\ldots \quad (2)$$

Now the quantity of light has been gauged, k' is eliminated from (1) and (2) and we get:

$$I = i^2 r \frac{U'_I}{U_i} \qquad \ldots\ldots\ldots \qquad (3)$$

Then the plate is removed, and the same I is thrown directly on the thermopile. We then get:

$$I = U_I k \qquad \ldots\ldots\ldots \qquad (4)$$

if U_1 denotes the deviation which the galvanometer now gets.

From (3) and (4) now follows:

$$k = \frac{i^2 r}{U_I} \frac{U'_I}{U_i} \qquad \ldots\ldots\ldots \qquad (5)$$

in which k again represents the quantity of energy required to impart the unity of deviation to the thermopile.

Now the thermopile and the galvanometer have been gauged.

As now the sensitiveness of Dr. MOLL's thermopile is variable over the width of the pile, it must be defined at the gauging of the pile which spot has been gauged. For the same reason it is not indifferent with what width of beam of light we work. To obtain an idea on both points, the sensitivity of the pile was determined as function of the width of the pile, and at the same time of the length of the pile.

For this purpose a very narrow beam of light, 0.2 mm. wide and 5 mm. long emitted by a Nernst-lamp, was thrown on the pile.

The rays fell at right angles to the latitudinal direction of the pile. The latter stood on a heavy block of wood, which could be displaced in a direction normal to the direction of the rays. A simple arrangement was applied to measure the displacements.

At every position of the piece of wood a number of readings were made of the deviation given to the galvanometer, when the beam of light fell on the pile. Then the pile was shifted vertically, so that another spot in the longitudinal direction of the pile could be treated. Also for the new longitudinal position the function of the latitude was determined.

At last the lines were obtained which are adjoined here.

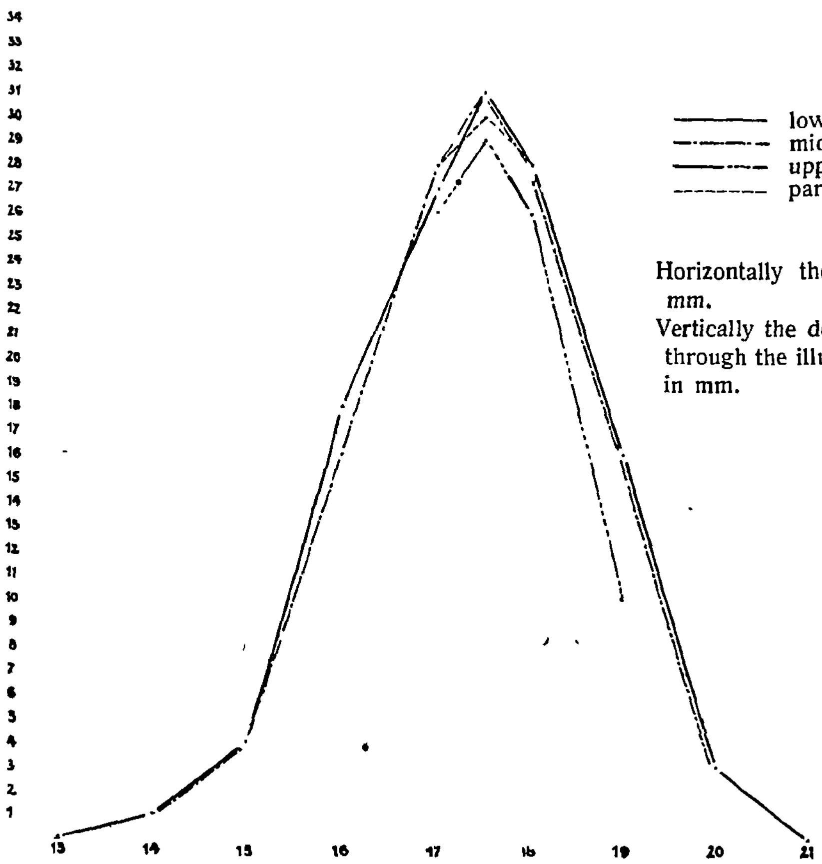
The thermopile was made in the year 1914 by the firm KIPP and SON at Delft (May, year 1914).

The thermoelements were made of copper-constantan. The pile was ± 20 mm. long and 8 mm. wide. The pile had to be repaired once, but showed still a sufficient uniformity.

It follows from the steep course of the curves how greatly the sensitiveness of the thermopile depends on the latitudinal direction of the pile.

	Lower part of the thermopile.										Middle part of the pile.								
Displacement in mm. normal to the direction of the rays of light.	13	14	15	16	17	18	17.5	19	20	21	13	14	15	16	17	18	17.5	19	20
Deviations of the galvanometer in mm.	0	±1	4	18	27	28	31	16	3	0		±1	4	16	28	28	31	16	3

	Upper part of the pile.										Part between the top and the middle.								
Displacements in mm. normal to the direction of the rays of light.					17	18	17.5	19							17	18	17.5		
Deviations of the galvanometer in mm.					26	26	29	10							28	28	30		



lower part of the thermopile
middle part of the thermopile
upper part
part between toppart and middle.

Horizontally the shiftings are indicated in mm.
Vertically the deviations of the galvanometer through the illumination of the pile, likewise in mm.

The necessity of sharp adjustment at a definite spot is very evident here. If e.g. we have gauged the thermopile at adjustment 16, and if we use the pile later at adjustment 17, it follows from the table that errors can be made of the order of 50°/₀, at least when again beams of 0.2 mm. are used.

Hence a displacement of only 1 mm. can already have a great influence. It is also clear that the deviation is greatly dependent on the width of the used beam of light.

When we consider e.g. 2 beams that send the same quantity of energy to the thermopile per second, the centres of which coincide in the maximum of sensitivity of the pile, but the widths of which differ, and may be successively 1 and 3 mm., it follows from the table that in the case of the narrow beam a deviation is obtained about 20°/₀ greater. In this calculation the mean values of the sensitivities have been used.

It follows further from the graphical representation that the thermopile has been made very uniform. The maximum sensitivities all lie at 17,5 mm. This uniform and sharp appearance of the sensitivity maximum enables us now to use this as criterion of adjustment.

The procedure in this is as follows: The function of width is determined with the beam to be used, as has been done above; from this it is possible to determine accurately with what adjustment the beam can show the greatest deviation. Then we adjust the thermopile in the required position, after which we carry out the desired measurements.

This operation, which can take place quickly, is carried out before the gauging as well as before the use of the thermopile.[1])

In this way the difficulties with the adjustment have been solved.

With regard to the width of the beams it may be observed that in these experiments use was made of a blackened platinum plate 1 mm. wide, which was at a distance of 1 mm. from the thermopile.

This plate can now be used in a simple way to make also the beams of light about 1 mm. wide.

In the gauging the used beam of light was obtained by cutting out by means of a screen from a larger parallel beam of light originating from a Nernstlamp. The screen is provided with screen doors, so that the beam to be used can be made broader and smaller.

[1]) With regard to this adjustment Dr Moll informed me lately, that for relative measurements he also works with the greatest sensitiveness, by rotating the thermopile to and fro. As a very accurate adjustment is necessary for the gauging, I prefer to determine for this the function of width in order to determine the maximum adjustment graphically from the different points that have been found.

When first we make the beam fall over the edges of the plate that is placed immediately before the thermopile, we see on the thermopile, besides the illuminated plate, 2 lines of light, with the shadow of the plate between them.

We now slide the doors towards each other, till the two lines of light have just disappeared from the thermopile, which can be very sharply observed. Accordingly the beam of light now falls exclusively on the plate before the pile.

When the thermopile is used the width is made equal to about one mm. in a corresponding way, only instead of screen doors use is made here of a cylinder lens.

With regard to the accuracy we observe that it follows from the table that 2 beams of equal intensity, but of the widths 1 and 0,5 mm., both adjusted at the maximum, will show about a difference of deviation of 2.5 %. It follows from this that if we perhaps make the widths equal to about 0.1 mm. in this way, no great errors will henceforth be made with this either.

The question whether the above given formulae may really be applied here, is fully entered into in my Thesis for the Doctorate. Nor will the constructions be discussed here, which were executed to my great satisfaction by the chief instrumentmaker of the laboratory, Mr. Joh. de Zwaan.

As a further elucidation of the investigation we shall proceed to give a numerical example.

Voltage of source of light	U'_I	U_I	U'_I/U_I	mean value
110 Volt	74.1 m.M.	172 m.M.	0.436	0.434
106 "	61.0 "	137.5 "	0.451	
102 "	47.3 "	109.0 "	0.434	
98 "	36.2 "	86.8 "	0.417	

i	U_i	Generated heat in cal. per sec. $i^2 r \times 0.24$	$\frac{i^2 r \times 0.24}{U_i}$ in $\frac{\text{cal.}}{\text{mm.}}$	mean value
0.015 amp.	179.9 m.M.	$0.015^2 \times 2.47 \times 0.24$	7.42×10^{-7}	7.40×10^{-7}
0.020 "	324.4 "	$0.020^2 \times 2.47 \times 0\,24$	7.30×10^{-7}	
0.025 "	500.4 "	$0.025^2 \times 2.47 \times 0.24$	7.49×10^{-7}	
0.030 "	720 "	$0.030^2 \times 2.47 \times 0.24$	7.41×10^{-7}	

By making the Nernstlamp burn at different tensions, the gauging could always be carried out for different intensities of light. Likewise different intensities of current were always used. These were measured in a milliampère meter of "Koeler". The resistance of the platinum plate was measured with the Wheatstone bridge.

The values 2,43 Ω, 2,50 Ω, and 2,48 Ω, hence on an average 2,47 Ω were found for r, the electric resistance.

$$k = \frac{i^2 r}{U_I} \times \frac{U'_I}{U_i} \quad \ldots \ldots \ldots \quad (5)$$

$$= 7.40 \times 10^{-7} \times 0.434 = 3.2 \times 10^{-7} \text{ cal. per second.}$$

i.e. that a deviation of 1 mm. is caused by 3.2×10^{-7} cal. per second. It should be stated here that the distance from the galvanometer mirror to the lath amounted to 174.3 mm. in these measurements.

I owe a few words of cordial thanks to Prof. Dr. W. Reinders, who enabled me to carry out this investigation in the Phys. Chem. Lab., and for the encouragement he gave me during the work.

Delft, July 15, 1917.