Physics. — *"An interpolation-formula for resistance-thermometry at low temperatures".* By Dr. F. ZERNIKE. (Communicated by Prof. H. HAGA).

(Communicated in the meeting of October 31, 1914.)

1. *Introduction.* In using resistance-thermometers to measure low temperatures with some accuracy one is often hampered by the difficulty to deduce the temperatures from the measured resistances.

This difficulty is partly due to a want of fixed points which could reproduce the absolute scale of temperatures with the required accuracy.

To a great extent the difficulty mentioned must be ascribed to the lack of an interpolation-formula which enables us to use a resistance-thermometer, after calibration at a few standard-temperatures, at all intermediate temperatures. For the following reasons such a formula is much more necessary in our case, particularly for the commonly used platinum-resistance than in that of most other physical measures.

First of all the resistance is not a "simple" function of the temperature, i.e. the higher derivatives of this function are large, which makes linear interpolation impossible even in small intervals, or quadratic interpolation in somewhat larger intervals. Ordinarily graphical interpolation will be used in such a case. However this will not remove the difficulty here, at least if an accuracy of $0.°01$ or $0.°02$ is required — as we shall suppose in the following. For a large scale drawing would then be required and the few known points would not allow to trace the curve unambiguously.

Some years ago considerations of this kind made me try the suitability to this purpose of many different formulae. I made use of the experimental data of ONNES and CLAY [1], in particular of those concerning the platinum wire Pt_I and the very pure gold wire Au_{III}. Temperatures were used after reduction to the thermodynamic scale and resistances reduced as far as possible to the values for pure metals by subtracting from everyone the resistance at the absolute zero, which was found by extrapolation. This was done in accordance with the well-known experiments of KAMERLINGH ONNES at the temperatures of liquid helium, which had refuted the current opinion that the resistance would become infinite at the absolute zero of temperature. Thus these experiments explained the failure of former attempts to find adequate formulae for the resistance

[1] Leiden Communications No. 95 and 99, these Proceedings 9, 207 and 10, 200.

at low temperatures [1]). However I did not succeed any better for a long time afterwards. It is now evident that this was caused by starting from the supposition, which seemed obvious, that the vanishing of the resistance in approaching the absolute zero had to be represented by a law of exponential character [2]). The principal difficulty was to represent by one single formula the resistances at the temperatures of liquid hydrogen together with those at higher temperatures. I wished however to maintain the condition that both regions should be represented .by one formula, in order to make possible an interpolation in the interval between the boiling-point of hydrogen and the melting-point of oxygen, where no measures with the gas-thermometer are available.

2. *Dependence for* T *small.* WIEN [3]) was the first to show the possibility of a different law for the resistance at the lowest temperatures in a paper in which from certain theoretical suppositions he deduced a decrease proportional to T^5. I verified at once that the hydrogen-temperatures would be much more closely represented by such a dependence than by exponential forms.

GRÜNEISEN [4]) has pointed out that the temperature-dependence of the product Tc_p shows a great resemblance to that of the resistance of the same metal, especially at low temperatures. He suggests further that both these quantities might be proportional to a universal function of T/T_0, the same for all metals, T_0 being a "characteristic temperature" of the metal [5]). The data available to test both these rules are, however, of much lower accuracy than that wanted here. Thus e. g. the specific heat-formula of DEBIJE [6]) could certainly yield a fair representation of the resistance, but not with an accuracy in any way comparable to that needed for resistance-thermometry.

It appears to me that the coincidence found by GRÜNEISEN may have a theoretical foundation. If such be the case the rule would

[1]) Compare the formulae with 5 and 6 constants to be found in different *Leiden Comm.* and also in the dissertation of Dr. CLAY, Leiden 1908.

[2]) This is also the case with the formulae of ONNES, Comm. 119, Proceedings **13**, 1093 and of LINDEMANN, Berlin Sitzungsber. 1911, 316, which do not aim at such a high accuracy.

[3]) Berlin Sitzungsberichte **1913**, 184

[4]) Verh. D. Phys. Ges. **15**, 186 (1913).

[5]) With respect to this point the result by MEISSNER, Verh. D. Phys. G **16**, 262 (1914) is interesting. According to his experiments the conduction of heat would show a wholly different value of T_0, somewhere like half the value for other phenomena.

[6]) Ann. d. Phys. (4) **39**, 789 (1912).

certainly hold the more exactly as the temperatures considered are lower. Thus I think it highly probable that the resistance vanishes proportional to T^4 at the absolute zero, as — according to DEBIJE — c_v vanishes in the same way as T^3. The following Table I shows that the resistance of gold at hydrogen-temperatures [1]) exhibits this proportionality with a fair approximation, if an additive resistance, caused by traces of impurities, is taken into account.

TABLE I.

T	Observed resistance Au	$0.2687 +$ $5.56 . 10^{-7} T^4$	Observed — Comp.
14.18	0.2910	0.2913	—0.0003
15.83	0.3037	0.3037	0
17.30	0.3190	0.3185	+ 5
19.00	0.3412	0.3412	0
20.35	0.3621	0.3644	—0.0023

3. *The new formula.* It is easy to put down an algebraic form which shall be proportional to T for large values of the variable T, but proportional to T^4 for very small values. A fraction such as

$$W = \frac{T^4}{aT^3 + bT^2 + cT + d} \quad \cdots \cdots \quad (1)$$

will do. For a large value of T we can develop into descending powers:

$$W = \frac{1}{a} T - \frac{b}{a^2} + \left(\frac{b^2}{a^3} - \frac{c}{a^2}\right) T^{-1} + \cdots \quad \cdots \quad (2)$$

for a small T into ascending powers of T:

$$W = \frac{1}{d} T^4 - \frac{c}{d^2} T^5 + \left(\frac{c^2}{d^3} - \frac{b}{d^2}\right) T^6 + \cdots \quad \cdots \quad (3)$$

From these formulae we see that the coefficient a determines the dependence at high temperatures, d that at low temperatures, while the coefficients b and c determine the way in which the two regions are linked together.

In representing the platinum-resistance it would seem advisable

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1) From KAMERLINGH ONNES and HOLST, Leiden Comm. 142 these Proceedings 17, 508.

to make use of the well-known fact that CALLENDAR's formula holds at higher temperatures, which simply means that the resistance can be represented there by a quadratic form of T. Therefore I tried to make formula (1) suitable for high temperatures by adding to the numerator a term $— kT^5$, in which k has to be determined from CALLENDAR's constant.

This very term seems to hinder a close fit at low temperatures. Now HENNING[1]) found later that at low temperatures CALLENDAR's formula did not deviate gradually from experiment, but that, on the contrary, it fits exactly down to 230° abs., deviating at once very markedly below this temperature. So it seemed useless to look for one formula suitable for both regions above and below that temperature, and I thus confined myself to test the unchanged formula (1) for temperatures below 230°.

Some tentative computations with the experimental material of KAMERLINGH ONNES and CLAY, and of HENNING, mentioned above, showed at once the suitability of the formula in question. Taking into account the additive resistance caused by impurities, the formula may be put thus:

$$W = \frac{C\tau}{1 + a\tau^{-1} + \beta\tau^{-2} + \gamma\tau^{-3}} + w \quad , \quad \ldots \quad (4)$$

'in which τ has been substituted for $0.01\ T$ to grasp easier the order of magnitude of the different terms. In (4) the coefficients a, β, γ do no longer depend on the particular value of the resistance, but merely 'on the inherent properties of the metal experimented on. Besides, impurities giving only approximately an increase in resistance which 'is independent of temperature, the constants a, β, γ will depend, though slightly, on the purity of the metal.

The computations gave for Pt as the best values of the constants something like:

a	β	γ
0.13	0.16	0.08
or 0.17	0.12	0.09

I did not undertake a more precise determination with the aid of. the data available, as the Leiden observers had announced the publication of a new calibration of the Pt-thermometer carried out in 1913.

4. *Determination of the constants.* In Leiden Communications N°. 141a[2]) KAMERLINGH ONNES and HOLST give the results of a very

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[1]) Ann. d. Phys. (4) **40**, 635 (1913).
[2]) These Proceedings **17**, 501.

accurate comparison, at a great · number of temperatures, of the platinum-thermometer designed by $Pt_{p'}$ · with the H_2 and He-thermometers, together with the reductions to the thermodynamical scale. Their figure 1, representing only the resistance above 56°, shows once more the peculiar way in which the resistance decreases when the temperature is lowered.

I started my computation from the corrected indications of the H_2-thermometer, designed by θ_{H_2} by the authors, and the corresponding resistances, both taken from their Table I. The absolute temperature of the freezing-point was assumed to be 273.09. In Table II I have inserted the values of T and W that have been used [1]).

In order to calculate the constants we put the formula thus:

$$\frac{T}{W-w} = a + b\tau^{-1} + c\tau^{-2} + d\tau^{-3} \quad . \quad . \quad . \quad . \quad (5)$$

Assuming a suitable value for w, we shall find from this formula four linear equations for $a, b, c,$ and d by using four temperatures. To begin with, a value of w may be found graphically. If another value of w is assumed, this changes only the left-hand side of the four equations (5). Thus the corresponding change of the unknowns is easily surveyed, and w is finally chosen in such a way that the formula gives the best approximation at a few other temperatures.

It was found undesirable to use more than one hydrogen temperature in the four equations. On the other hand we cannot do without one such a low temperature if we want to determine c and d accurately.

From the four temperatures $T = 170.39, 90.27, 60.57$ and 20.42, I found, taking $w = 1.26 \,\Omega$, the values of the unknowns given as "first approximation" in Table III. From these were computed the remaining discrepancies at the other temperatures. A second approximation was next found from the same equations, changing the constant terms so as to get small deviations at the temperatures 170, 90, 60, and 20, at which the first approximation naturally fitted exactly. Thus the deviations could easily be distributed more evenly. The resulting constants have again been inserted in Table III, whereas Table II gives under the heading W_2 the resistances calculated therefrom, the next column showing the deviation from experiment.

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[1]) The values at the last four temperatures in Table II have not been used; that at 77.91 was excluded because of an obvious printer's error in the original paper. This error has been corrected here after the indication of Prof. Onnes.

TABLE II.

T	W observed	W_2 computed	$W-W_2$	W_d computed	$W-W_d$	Corresponding ΔT
	Ω	Ω .	$10^{-4}\,\Omega$	Ω	$10^{-4}\,\Omega$	$0^\circ.001$
14.70	1.453	1.45406	— 10.6	1.45385	— 8.5	+ 16
16.04	1.531	1.53201	— 10.1	1.53184	— 8.4	+ 13
17.01	1.601	1.59983	+ 11.7	1.59969	+ 13.1	— 17
18.04	1.685	1.68326	+ 17.4	1.68317	+ 18 3	— 21
19.45	1.819	1.81786	+ 11.4	1.81784	+ 11.6	— 11
20.43	1.924	1.92624	— 22.4	1.92626	— 22.6	+ 19
56.93	15.119	15.1255	— 65	15.1260	— 70	+ 13
60.57	17.097	17.1026	— 56	17.1027	— 57	+ 10
68.38	21.491	21.4859	+ 51	21.4847	+ 63	— 12
86.36	31.904	31.9010	+ 30	31.8966	+ 74	— 13
90.27	34.180	34.1808	— 8	34.1759	+ 41	— 7
142.66	64.189	64.2008	— 118	64.1969	— 79	+ 14
159.53	73.629	73.6366	— 76	73.6361	— 71	+ 13
170.39	79.674	79.6655	+ 85	79.6676	+ 64	— 12
193.52	92.422	92.4111	+ 109	92.4196	+ 24	— 4
211.59	102.280	102.2987	— 187	102.3115	— 315	+ 58
230.00	112.278	112.3206	— 426	112.3407	— 627	+ 115
273.09	135.450	135.6372	— 1872	135.6754	— 2254	+ 418
77.91	26.988	26.9797	+ 83	26.9771	+ 109	— 19

5. *Computation with least squares.* In order to get my final solution I yet applied corrections determined by the method of least squares to the values found for w, a, b, c, and d, though it was hardly to be expected that the experimental values would thus be represented much closer. Thence the rather lengthy computation was principally made for another reason, viz. for the determination of the weights of the unknowns. Indeed the preceding calculations showed clearly that the constants b and c could not be found very accurately from the data, a small change of the constant terms of the equations causing a great deviation in the unknowns.

The form (5) could not be used for the least-square solution, as the left-hand side of that formula is known with greatly different accuracy at the different temperatures, while w has also to be corrected. Thus the only expedient is to use the differential formula, and this implies a rather accurate couple of values of the unknowns to start with. Therefore the second approximation could not be dispensed with.

In computing resistances from formula (5) it is most convenient to transform it as follows:

$$W = \frac{100}{a\tau^{-1} + b\tau^{-2} + c\tau^{-3} + d\tau^{-4}} + w \quad . \quad . \quad . \quad (6)$$

Herefrom we find as the form of the equations of condition:

$$\Delta w + \Delta a\tau^{-1}\left(\frac{W-w}{100}\right)^2 + \Delta b\tau^{-2}\left(\frac{W-w}{100}\right)^2 +$$

$$+ \Delta c\tau^{-3}\left(\frac{W-w}{100}\right)^2 + \Delta d\tau^{-4}\left(\frac{W-w}{100}\right)^2 = W - W_2$$

in which Δa, Δb, Δc and Δd are *negative* corrections.

At the temperatures of liquid hydrogen one same change of resistance corresponds to a change of temperature from 5 to 6 times larger than at the higher temperatures. For that reason a weight 30 was given to the 6 corresponding equations of condition, taking the weight of the 9 other ones as unity.

The corrections found from the normal equations were applied to the constants of the second approximation, thus yielding the final solution stated in Table III. The weights found for these quantities have been inserted in the following line of that table. It will be seen at once from these weights that b and c cannot be determined accurately. The mean errors have been derived from the weights by assuming the mean error of a single resistance somewhat arbitrarily as $\pm 0.001 \, \Omega$. Comparing these mean errors, stated in the fifth line of Table III, with the quantities themselves, to which they belong, it might seem that these quantities have been given far too accurately. Such is indeed the case, if the constants found are merely to be compared with numbers of the same kind calculated from other experimental data. It is quite another thing however if the constants are to be used for interpolation, i.e. for the investigated thermometer itself. Then they ought not to be rounded off any more, as in that case other mean errors apply that are given in the lowest line of Table VI. These give namely the precision of each unknown *separately*, i. e. *if a definite value is assumed beforehand for the other unknowns*. The weights from which these errors have been

derived are simply equal to the coefficients of each unknown in its own normal equation.

TABLE III.

	w	a	b	c	d
First approximation	1.245	1.881	0.2946	0.2348	0.18046
Second approximation	1.249	1.8868	0.2852	0.2388	0.18046
Final solution	1.24874	1.884918	0.289523	0.236524	0.180648
Weights	32.7	33 5	4.94	7.53	55.6
Mean error	±.00018	± 000173	± 000450	±.000364	± 000134
m. e. for formula	7	14	21	26	20

6. *Result.* Finally Table II shows the comparison of the resistances computed from the definitive constants, with the experimental values. It will be seen from the column for $W-W_d$ that the observations are represented a little better still. The sum of the squares of the deviations shows a decrease from 87 to 72. In the last column the quantities $W-W_d$ have been transformed into the equivalent differences of temperature. Now the uncertainty of a determination with the gas-thermometer is stated to be $0.°02$, from

TABLE IV.

T	W	$\angle W$	$\Delta^2 W$	T	W	ΔW	$\Delta^2 W$
10	1.2966			120	51.3535		—0.0439
		0.5806				5.6938	
20	1.8772		+1.2563	130	57.0473		411
		1.8369				5.6527	
30	3.7141		1 4868	140	62.7000		373
		3.3237				5.6154	
40	7.0378		1.1854	150	68.3154		329
		4.5091				5.5825	
50	11.5469		0.7336	160	73.8979		289
		5.2427				5.5536	
60	16.7896		3780	170	79.4515		254
		5.6207				5.5282	
70	22.4103		1608	180	84.9797		219
		5.7815				5.5063	
80	28.1918		+ 454	190	90.4860		193
		5.8269				5.4870	
90	34.0187		— 109	200	95.9730		168
		5.8160				5.4702	
100	39.8347		349	210	101.4432		150
		5.7811				5.4552	
110	45.6158		434	220	106.8984		— 0.0129
		5.7377				5 4423	
120	51.3535		—0.0439	230	112.3407		

which we conclude that our *formula represents all points below* 200° *within the errors of observation* [1]).

TABLE V.

T	W	T	W	T	W
1	1.24875	55	14 1022	73	24.1347
2	1.24883	56	14.6307	74	24.7118
3	1.24917	57	15.1637	75	25.2900
4	1.25008	58	15.7016	76	25.8691
5	1.25197	59	16.2436	77	26.4489
6	1.25534	60	16.7896	78	27.0294
7	1.26079	61	17.3392	79	27.6104
8	1.26898	62	17.8922	80	28.1918
9	1.28064	63	18 4484	81	28.7738
10	1.29657	64	19.0074	82	29.3561
11	1 31758	65	19.5691	83	29.9386
12	1.34454	66	20 1333	84	30.5213
13	1.37831	67	20.6997	85	31.1041
14	1.41978	68	21.2682	86	31.6871
15	1.46981	69	21.8385	87	32.2701
16	1.52926	70	22.4103	88	32.8531
17	1.59896	71	22.9838	89	33.4360
18	1.67968	72	23.5586	90	34.0187
19	1.77219				
20	1.87715				
21	1.99519				
22	2.12687				

A few words about the temperatures above 200°. There the deviations are seen to increase rapidly. If we had used the proportions $W/W_{273 \cdot 09}$, instead of the resistances themselves — as

[1]) Yet it will be noticed that the deviations, at least those at liquid oxygen temperatures, are not distributed at random, but show a regular course. From this we draw the conclusion, interesting in itself, that the mutual agreement of these measurements is much better than would be indicated by an accuracy of 0°.02. Surely this only tells something about the purely accidental errors.

it is often done, in order to construct the formula such that it identically equals 1 at the freezing-point — it would have been impossible to obtain the close agreement at low temperatures.

Besides I give the constants for formula (4), which may be useful in comparing the results for other Pt-wires with the data used here. These constants can evidently be found from b, c, and d by division by a:

α	β	γ
0.1536	0.1255	0.0958

A survey of the course of W, as it follows from our formula, is given in Table IV, in which we find W for every ten degrees, with first and second differences. The same numbers which served for this computation, were also used for the ten times smaller temperatures of Table V.

It will be seen from the first numbers in that table, that even at helium-temperatures the formula is in a sense in accordance with experiment, yielding a resistance invariable within the errors of observation. However it may very well be that more accurate measurements in that region will show rather large deviations from the formula. Indeed our formula is based on the assumed behaviour of the resistance of *pure* metals at the absolute zero, which appeared probable partly on theoretical grounds, and may also be expressed thus: the resistance and its first three derivatives with respect to T vanish at $T = 0$. Now I only dropped the first of these four conditions in the application to a slightly impure metal, whilst it seems possible, in view of the results for constantin and manganin, that at least also the second one, $dW/dT = 0$, is no longer exactly satisfied as soon as impurities are present. Therefore the accuracy of the four assumptions can only be tested experimentally by comparing wires of different degree of purity.

Further Table V gives a part of a table for every degree, as it would be calculated from the formula for practical use. The numbers given have been obtained from Table IV by interpolation *with third differences*. Even this did not yield the exact value for the first five temperatures, 55° to 60°. Therefore they have been computed downright from the formula. On the other hand the interpolation becomes much simpler above 90°.

7. *Application of the formula to other metals.*

In what is mentioned above the suitability of the new formula has been tested for the most important case in practice, that of the

Pt-resistance for which more accurate measures at more points are available than for any other metal. Still it may be of interest to mention also the results obtained with the formula for two different gold-wires and for mercury. Table VI shows the values of the constants, together with the deviations from experiment [1]).

	w	a	b	c	d
Au_I	0.265	0.2056	0.04218	0	0.01425
Au_{II}	0.5700	0.2646	— 0.040	0.0569	0.00186
Hg	0	9.360	0.437	0.0568	0.00146

TABLE VI.

T	Au_I computed	Observed — Comp.	T	Au_{II} computed	Observed — Comp.	T	Hg computed	Observed — Comp.
		0.0001			0.0001			0.001
14.18	0.2908	+ 2	14.16	0.6108	+ 40	4.19	0.0581	— 2.1
15.83	0 3039	— 2	15.79	0.6272	+ 14	4.27	0.0614	-- 1.4
17.30	0 3190	0	17.00	0.6416	+3	4.33	0.0639	— 0.3
19.00	0.3408	+ 4	17.96	0.6542	0	4.37	0.0656	0
20.35	0.3618	+ 3	19.35	0.6756	— 7	14.57	0.939	0
65.18	2.2906	— 5	20.31	0.6916	— 5	15.78	1.067	+ 2
72.58	2.6763	0	20.48	0.6946	0	17 89	1.294	+ 4
83.31	3.2309	+ 3	68.22	2.6093	0	20.39	1.563	0
87.99	3.4710	0	78.28	3.0917	0	80.92	8.100	—14
90.75	3.6117	— 7	90.27	3.6549	0	90.13	9.088	0
						116.52	11.914	+86

Above 100° the deviations for *Hg* increase gradually, just as for *Pt* above 200°. The close agreement in the region of liquid hydrogen, however, is remarkable. The computed curve has been drawn through both extreme temperatures of that region, through a much lower one and through a much higher one, and by that means it gets automatically the required curvature in the hydrogen-region. This is especially remarkable as the curvature appears to be practically zero.

[1]) Au_I and Hg after the experiments of ONNES and HOLST, Leiden Comm. 142a, these Proceedings 17, 508, Au_{II} from KEESOM and ONNES, Comm. 143, Proc. 17, 894.

The greater deviations for Au_{II} at the lowest temperatures should be ascribed to the influence of impurities. The greater value of w already is an indication that Au_{II} is much less pure than Au_{I}. Further the same remarks apply here that have been made in § 6 about the resistance of Pt at helium-temperatures.

Physics. — *"The magnetic rotation of the plane of polarisation in titane tetrachloride"*. II. By Prof. L. H. SIERTSEMA. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of October 30, 1915).

In a preceding communication [1]) the results have been recorded of observations on the negative magnetic rotation of $TiCl_4$ for different wavelengths, and an investigation was announced on the question whether the dispersion of rotation agrees with ,what was to be expected according to theory.

The theories of the magnetic rotation bring it in connection with the ZEEMAN-effect, and lead to formulae in which the rotation is represented as the sum of a number of terms, each corresponding to a free vibration of the substance. Similar formulae also hold for the index of refraction. An investigation as to whether the observations are in harmony with the theory will, therefore, have to lead to the drawing up of formulae of the form required by the theory, representing the observed indices of refraction and constants of rotation, and containing in both cases *the same* free frequencies.

For the theoretic formulae we shall have to start from those which have been derived by LORENTZ in the Encykl. der math. Wiss. [2]), which will, however, be subjected to some modifications.

First of all we can keep in view that we shall only apply the formulae for wavelengths far from a free vibration, and that therefore we need not take absorption into consideration. This renders it possible for us to put the constant g in the formulae in question zero, which simplifies them considerably.

In another respect extension is, however, necessary. As here the formulae will be applied to liquids it is no longer allowed in the computation of the force acting on a charged particle to neglect the term proportionate to the polarisation, which must be added to the

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[1]) These Proc. XVIII p. 101.

[2]) LORENTZ. Theorie der magneto-optische Phänomene. Encykl. d. math. Wiss. V. 3, p. 199.