Physics. — *"On the change of the resistance of the metals at very low temperatures and the influence exerted on it by small amounts of admixtures"* I. By Prof. H. KAMERLINGH ONNES and J. CLAY. Communication N°. 99[c] from the Physical Laboratory at Leiden.

(Communicated in the meeting of June 29, 1907).

§ 1. *Introduction.* In Comm. N°. 99[b] we called attention to the very large differences in the change of the galvanic resistance with the temperature, which different platinum wires show when we descend to the low temperatures which are to be reached with liquid hydrogen. Such differences were still more pronounced for different gold wires which we investigated. With this metal (see Comm. N°. 95[d] These Proc. Sept. 1906) we had taken in hand the investigation of the influence of small amounts of admixture announced in Comm. N°. 77, because the influence of admixing silver would probably be important and the percentage of silver could be determined very accurately, the possibility of drawing out wires of the different kinds of gold and its high melting point moreover rendering this metal preferable to the for the rest very suitable mercury.

Besides, the inquiry into the influence of small amounts of admixture on the change of the resistance of gold with the temperature proved at once useful as we thought that the gold resistance thermometer would be preferable to the platinum resistance thermometer. Dr. C. HOITSEMA, who already obliged us before (see Comm. N°. 95[d]) by putting pure gold at our disposal, has had the kindness of supplying us again with different samples of gold of high purity, further of preparing for us different alloys with accurately known small percentages of admixture, and of determining the impurity which was finally left in the wires after they had been melted down. For all this valuable help and for the information which Mr. HOITSEMA was enabled to give us by his wide experience we express our hearty thanks.

The investigation of the different gold wires with very small amounts of admixture may of course also be considered as the calibration of different gold resistance thermometers. (Comp. Comm. N°. 99[b] § 1). We prefer, however, to consider it as a part of our more general investigation (Comm. N°. 77) on the change of the resistance with the temperature for pure metals, and on the influence which small amounts of admixture exert on it.

As to the change of the specific resistance for the pure metals reduced to the most normal state, attention is drawn to the temperature of the

point of inflection $\frac{d^2r}{dT^2}=0$ the temperature of the *point of proportionality* $\frac{dr}{dT}=\frac{r}{T}$ and the temperature of the *minimum* $\frac{dr}{dT}=0$. It is clear that the situation of these points, and the correspondence[1]) and difference of their situation and of the coefficient of variability of the resistance with the temperature in general for different metals of different classes must furnish important data for the theory of electrons.

The investigation of these points is only possible by the aid of liquid hydrogen. Only in some cases — and even then the purity of the metal is open to doubt — the point of inflection, whose existence was indicated by DEWAR, was found high enough to be ascertained without measurements for hydrogen temperatures. For metals in the purest and normal state the point of proportionality lies probably still below the temperatures which are to be reached with liquid hydrogen. It is true that DEWAR derived from his measurements at two hydrogen temperatures that it was surpassed for some of his metal wires. Our measurements, however, point to this that as a metal is brought to a purer and more normal state, the point of proportionality is found to be lower. The metal wire which came nearest to this *ideal* state, was one of our gold wires. Even at the lowest temperature the point of proportionality was not yet reached for that wire. Probably DEWAR's wires were further removed from this ideal state.

With the low situation which we find for the point of proportionality measurements at two hydrogen temperatures do not suffice, but we have made determinations at at least three hydrogen temperatures, because they were necessary to determine the probable situation of the point of proportionality by the aid of $\frac{d^2r}{dt^2}$. Until we have reached the proportional point, we need not discuss the question of the minimum point.

In the inquiry into the properties of the metals in the ideal state we must know first of all in how far the metal is in this state, and else how we can derive what would be found in this state. The influence of small deviations in the nature of the metals on the change of the resistance with the temperature, becomes so exceedingly great for the hydrogen temperatures, that a special investigation is necessary for them. Here two things have to be paid attention to: to small amounts of admixture, and to differences in

[1]) In this respect something is to be derived from the formulae given by us in this and in the preceding communications.

hardness etc. For the present we have left the latter out of account; in the investigation of the influence of the admixtures, however, the influence of the hardness was as much as possible eliminated by our treating the different samples of metals exactly in the same way when comparing them, and by reducing them to the same state of softness.

The most natural explanation of the whole of the results obtained as yet (in this and the preceding Communication) is to ascribe the deviations for the different wires of one and the same metal to impurities in the metal, which may also come in during the drawing if efficient precautions do not prevent it, and which even in very small quantities exert a very great influence on the changes of the resistance with the temperature.

The influence of the drawing is altogether lost for mercury, in which it is also easy to ensure uniform distribution of small quantities of admixture. This enhances the importance of the study of this metal for the investigation of the influence of admixture. In the first place we have measured its resistance at hydrogen temperatures which had not yet been determined; it is given in § 4. It proved that for pure mercury [1]) the inflection point falls in the region of liquid hydrogen temperatures. This is a drawback for the inquiry into the change of the resistance with the temperature for pure metals.

Just as the gold wire Au_V (see § 2), also the silver wire Ag_I and the platinum wires of the preceding Communication are probably purer than DEWAR's wires of the same metals. For bismuth, on the other hand, DEWAR has most likely had a purer sample than we. The change of the resistance at hydrogen temperatures for this metal, which had not yet been measured by him, has been given in § 5. The observations for lead for those temperatures, which were still wanting up to now, have been given in § 6.

The high degree of purity for some of the metals which were at our disposal, and the lower temperatures to which we descended (solid hydrogen evaporating at 2,5 m.m. pressure) render the decrease of the resistance in some cases many times larger than was observed by DEWAR. To this it is also owing that we have observed the great influence, which very small changes in the nature of the metal obtain on the change of the resistance at hydrogen temperatures. We may account for this by paying attention to the difference of the resistance of a wire of pure metal at the temperature T, r_T, with

[1]) Perhaps in connection with the low melting point. Possibly the point of proportionality is first reached for osmium.

that of a wire of the same metal with a proportion of admixture x at the same temperature, r_{xT}. According to a theorem of MATTHIESSEN[1]) derived from observations between 0° and 100°, this difference (the theorem refers to a difference that is about the same as that considered here) is constant for different temperatures. FLEMING[2]) found this theorem about confirmed down to — 200°. As we have found, this theorem no longer holds for hydrogen temperatures. But the deviation is not of such a nature as to affect our conclusions. So if to form an idea of the influence of the admixtures, we put $r_T = r_{iT} + px$, further p constant and large, then it is clear that — when r_{iT} becomes as small as is the case (see Table I Au_V) for pure metals and hydrogen temperatures — the resistance of a metal for the case that x gets an appreciable amount, will be owing almost exclusively to the admixture. The small amounts of admixture obtain a remarkable influence[3]).

Analogues are easily found in the important influence of small amounts of admixture on the density in the neighbourhood of the critical temperature of a substance, in a space becoming opaque by a cloud depositing on a minimum quantity of dust. But for a further discussion the systematic investigation of the influence of small amounts of admixture should be more advanced. At all events the changes of the resistance with temperature at hydrogen temperatures proves to be a highly sensitive criterion to decide about the nature of a metal.

§ 2. *Gold.* The different samples of pure gold were all supplied by Dr. C. HOITSEMA. With the exception of two the wires were all treated in exactly the same way, drawn out by HERAEUS to 0,1 mm. diameter, and treated at every pull with diluted sulphuric acid and nitric acid. The gold wire Au_{VI} was drawn in a different way and made strongly impure. The exact amount has not yet been ascertained.

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1) Pogg. Ann. Bd. CXXII.

2) Proc. Royal Institution June 1896 p. 9.

3) To a less degree of purity of the examined metal wires it is perhaps to be ascribed that NICCOLAI, Att. Linc. 16, 1st sem. p. 906 finds a smaller decrease of resistance at — 189° than we do, as appears by comparison with Tables I, III, V of this communication and V of Comm. N°. 96b. Indeed NICCOLAI finds:

	silver	gold	lead	platinum
0°	1	1	1	1
— 189°	0.2784	0.3068	0.3357	0.3198

[Added in the translation].

Au_0 is the wire which was calibrated in Comm. N°. 95^d. After melting it down Dr. HOITSEMA found 0,03% impurities. As to the wires Au_{III}, Au_{IV} and Au_V, Dr. HOITSEMA found about 0.015% admixture for Au_{III}, about 0.005% admixture for Au_{IV} and Au_V. Au_{Ag1} was made of an alloy which after the wire had been remelted, contained 0.4% admixture (probably chiefly silver). Wound round the same glass cylinder all wires except Au_0 and Au_{Ag1} were heated at the same time in an annealing furnace for a long time, and slowly cooled, as had also been done with Au_0 and Au_{Ag1}, so that they were perfectly malleable.

In table I the resistances have been given expressed in that at 0° as unity. These were about 9Ω.

TABLE I.

Change of the resistance of different gold wires with the temperature.

Temperature	Au_{III}	Au_{IV}	Au_V	Au_{VI}	Au_0	Au_{Ag1}
0°	1	1	1	1	1	1
—103.83	0.59601	0.59389	0.59306	0.64827	0 60545	0.64549
—183.00	0.27653	0.27177	0 27096	0.37053	0.30070	0.37099
—197.87	0.21456	0.20963	0.20871	0.31659	0 23908	
—205.01			0.17897		0.20992	
—215.34	0.14058	0.13407	0.13337	0.16822	0.16681	
—252.93	0.01602	0.008743	0.008103	0.13669	0.04554	0.13942
—255.13			0.005691			
—258.81	0.01095	0.004265	0.003601	0.13241	0.03982	0.13288
[—261]			0.002713			
[—262]		0.003257	0.002526			

To facilitate comparison we may observe that DEWAR found 0.03290, whereas we found 0.008103 at — 252°.93 for Au_V.

§ 3. *Mercury.* It was doubly distilled and brought into a glass spiral. The latter was protected by a bath of pentane, which was slowly cooled from the bottom upwards before it was immersed into the bath of the cryostat. We found:

TABLE II.

Change of the resistance of pure mercury with the temperature

Temp.	Resistance
0°	97 126
— 183 00	7 2650
— 197 87	6 0103
— 205 01	5 3900
— 215 34	4.5057
— 252.93	1 2613
— 258.81	0 7534

§ 4. *Silver.* This was also supplied by Dr. C. HOITSEMA and drawn to a wire of 0.1 m.m. by HERAEUS, during which operation it was treated in exactly the same way as the gold and the platinum. After the resistance had been determined, the composition was controlled; the silver contained then 0.18% impurity. The zero point

TABLE III.

Change of t e resistance of silver with the temperature.

Temperature	Resistance Ag_1	$O-C_D$	$O-C_{AIV}$
99°.76	1.41089	0	0
0 before	1	0	0
0 after	1 00037		
— 103.81	0.58087	— 0 00042	— 0.00042
— 139.87	0 43282	+ 42	+ 42
— 183.57	0 24679	— 17	0
— 195.17	0 19703	+ 29	— 2
— 204.67	0 15528	— 31	
— 252.92	0.008913	0	
— 259.22	0.006 42	0	

of the silver wire (resistance at 0°) changes slightly by being drawn out in consequence of the difference in expansion of silver and glass. The preceding table gives the resistance expressed in that at 0° as unity. (The resistance at 0° was 21.519 Ω).

Column $O—C_D$ contains the deviations from a formula adjusted from $+100°$ to $-259°$ of the new form:

$$\frac{W_t}{W_0} = 1 + a \,.\, 10^{-2} \,.\, t + b\, 10^{-4} t^2 + c\, 10^{-6} t^3 + d\left(\frac{10^6}{T^3} - \frac{10^6}{(273.09)^3}\right) + e\left(\frac{10^{10}}{T^5} - \frac{10^{10}}{(273.09)^5}\right) \quad . (D)$$

which agreed best with the values:

D	a	b	c	d	e
Ag_I	+0.402746	+0 001355	+0.004806	+0 00955	−0.000013

For a comparison with platinum and gold the column $O—C_{A_{IV}}$ gives the deviations from a formula of the form A (see Comm. N°. 95c and 95d):

$$\frac{W_t}{W^0} = 1 + a.t\, 10^{-2} + b.t^2.10^{-4} + c.t^3.10^{-6} + d\left(\frac{10^2}{T} - \frac{10^2}{273.09}\right)$$

with values which we distinguish by A_{IV} on account of the other way of adjusting the coefficients.

A_{IV}	a	b	c	d
Ag_I	+0.40355	+0.03968	+0.005232	+0.008662

§ 5. *Bismuth.* The measured resistance, which we shall also investigate in the magnetic field, was that of a bismuth spiral of HARTMAN and BRAUN N°. 301. The resistance expressed in that at 0° as unity (the resistance at 0° was 17.3138 Ω) was:

TABLE IV.

Change of the resistance of Bismuth with the temperature.

Temperature	Resist nce Bi_I	$O-C_{A_{III}}$
12°64	1.05148	0
12°70	1.05165	
0	1	
— 103.71	0 63649	+ 0.00952
— 139.88	0.52865	— 127
— 164.05	0 46246	— 144
— 182 73	0 41435	— 69
— 195.17	0.38478	+ 144
— 204 68	0 36064	+ 127
— 216 01	0 33014	— 69
— 253 01	0 22329	— 92
— 255 34	0 21388	— 2
— 258 86	0 19574	0

This column $O-C_{A_{III}}$ gives the differences with a formula of the form A (see § 4), with values which we shall indicate by A_{III} on account of the adjustment at two hydrogen temperatures and over the region to 0°:

A_{III}	a	b	c	d
Bi_I	+0.393037	+0 051928	+0.0038155	—0.0079700

§ 6. *Lead.* The knowledge of the resistance of lead is of particular importance on account of the fact that this metal does not show the THOMSON-effect. Probably the lead used by us, contained no more than 0,015 % admixture.

The resistance of a narrow strip cut out from the flatted lead and protected against chemical action by paraffine expressed in the resistance at 0° (3.18114 Ω) as unity was found to be:

TABLE V.

Change of the resistance of lead with the temperature.

Temperature	Resistance
+ 16°.33	1 0652
0°	1
—103.63	0 59548
—183.65	0.29439
—195.15	0.25257
—204.52	0.21742
—216.61	0.17129
—252.78	0.03032
—255.07	0.02314
—258.70	0.01311

Physics. — *Repetition of* DE HEEN's *and* TEICHNER's *experiments on the critical state"*, by Prof. H. KAMERLINGH ONNES and G. H. FABIUS. Communication N°. 98 from the Physical Laboratory at Leiden.

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§ 1. *Introduction.* Experiments have been repeatedly made from which the conclusion was drawn, that a substance can assume different densities above its critical temperature with the same pressure and the same temperature, which densities it can retain for hours according to some investigators [1]). That in reality this is not the case, and that the

1) TRAUBE Ztschr. f. phys. Chem 58 p. 477. 1907, cf. also MATHIAS, Le point critique des corps purs p. 250.

When with change of density dissociations or variations of volume of the molecules themselves should made their appearance which clearly require more time than the establishment of temperature equilibrium through conduction of heat and convection, we should when a phase was kept at constant volume after having suffered variation of density, have to find an increase of the pressure both for liquid and vapour phases and for phases above the critical temperature; thermodynamically it follows from this that the density of liquid in equilibrium with vapour would then have to be a function of the time.

Cf. TRAVERS and USHER on variations of density in consequence of false equilibria.