Physics. — *"Isotherms of mon-atomic substances and their binary mixtures.* XXV. *The same of di-atomic substances.* XXXI. *The compressibility of hydrogen- and helium-gas between* 90° *and* 14° *K.*" By F. P. G. A. J. VAN AGT and H. KAMERLINGH ONNES. (Comm. N°. 176*b* from the Physical Laboratory at Leiden).

(Communicated at the meeting of June 27, 1925).

§ 1. *Introduction.* The investigation of the compressibility of hydrogen- and helium-gas at the boiling-point of hydrogen made by PALACIOS MARTINEZ and KAMERLINGH ONNES (Comm. Leiden N°. 164) has been continued by us particularly at lower temperatures. Also some measurements have been made at the same and at higher temperatures. All the measurements were differential, a method which unexpectedly did not succeed in the first mentioned investigation, as the pressure difference between the hydrogen- and the helium-sides for the high densities appeared to be too great for simultaneous pressure-measurements of both gases. Finally the contents were interchanged in order to investigate if possible asymmetries in the apparatus could influence the results.

The new experiments were especially made for the purpose of determining accurate values for the second virial-coefficient in the empirical equation of state

$$pv = A + Bd + Cd^2 + Dd^4 \text{ etc. }^{1)}$$

in order to verify and extend the determinations of the same quantity of KAMERLINGH ONNES and DE HAAS. (Comm. Leiden N°. 127).

In the case of the smaller densities, which were used in our measurements ($d_A \leqq 12$) the influence of the coefficients from C on could be neglected, so that our method was particularly adapted for accurate determination of the *B's*.

With the *B*-values obtained it was possible to calculate the corrections for reducing the scales of the international hydrogen- and helium-thermometers to the Avogadroscales of these gases.

§ 2. *The apparatus.*

This was practically the same as that used by PALACIOS MARTINEZ and KAMERLINGH ONNES, discussed in their above-mentioned communication. Only the couplings in the capillaries connecting the pipettes to the thermometer were removed, and the ends of the capillaries soldered

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1) Comm. Leiden N°. 71.

together. Though this made it somewhat less easy to dismount the apparatus, we decided to do it, after the lead-packing in these couplings, after having kept well closed for some time, began to leak at the most unsuitable moments. The new thermometer T_8 took the place of T_3, which was accidentally broken. Later thermometer T_7 was replaced by T_9 for the measurements below the boiling-point of hydrogen, for, as already mentioned in § 1 PALACIOS MARTINEZ and KAMERLINGH ONNES did not succeed in measuring differentially the third and fourth densities because of the great pressure difference in the thermometers. By replacing one thermometer by a somewhat smaller one of a volume previously accurately calibrated, we succeeded in measuring, differentially, the four densities for hydrogen and helium at the same time.

The volumes of the new thermometers were:

$$T_9 = 103.195 \text{ cM}^3 \qquad T_8 = 110{,}431 \text{ cM}^3.$$

After the whole apparatus had been dismounted, new measurements of the dead space volumes were necessary. For these we obtained:

$$v'_1 = 0.762 \qquad v_1 = 0.772$$
$$v'_m = 0.066 \qquad v_m = 0.067.$$

A thermo-regulator, filled with methyl-chloride, was first used, to maintain a constant temperature in the waterbath containing the pipettes for the pressure determinations at room-temperature. Later the same result was obtained by surrounding the water-bath with a thick mantle of very porous rubber wich did not allow the room-temperature, differing only slightly from the bath-temperature, to change too much. In this way the use of the regulator, generally a difficulty, could be avoided. The following figure represents the result of the method.

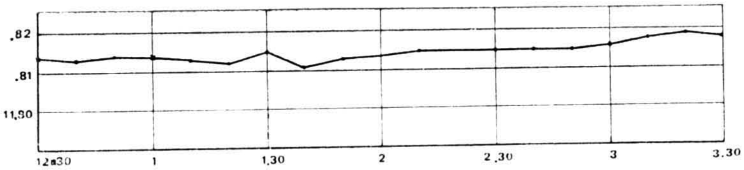
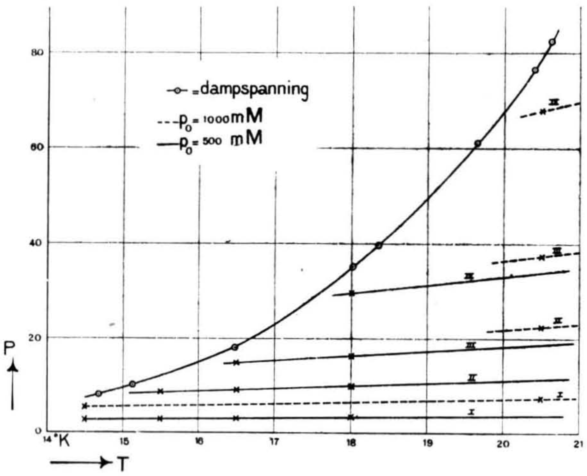


Fig. 1.

§ 3. *Measurements and calculations.*

These were made in the same way as communicated in detail in Comm. N°. 164.

In the case of the determinations at the boiling-point of hydrogen the thermometers and pipettes were filled with ± 1000 mM. hydrogen and helium (zero-pressure) whilst for the measurements below the boiling-point it was necessary to reduce this pressure to about one half in order to avoid condensation of the hydrogen. This made it possible (see fig. 2) to measure at ± 18° K. with 4, at ± 16,5° K. with 3, at ± 15,°5 K. with 2 densities, and even at 14,°5 K. a measurement with the smallest



dampspanning = vapour tension.
Fig. 2.

density (d_A = ± 0.7) could be made, which could be combined with a determination at about the same temperature with the international hydrogen thermometer, of about twice the density.

Because of the size of the apparatus a smaller zero-pressure was not possible.

Afterwards measurements with the contents interchanged were made with the same zero-pressure and at ± 18° K, so that here also 4 densities could be worked with. The thermometers and pipettes were very carefully exhausted and washed before filling with the new and interchanged gases. The measurements could again be made simultaneously for both sides to the greatest density included.

For the calculation of pressures, virial-coefficients and densities we refer to Comm. N⁰. 164 (pag. 22).

The following data underlie the calculation of the virial-coefficients at the temperatures of the waterbath.

Hydrogen 1)		Helium 2)	
$A_{A\,0^\circ\,C.}$	0.99942	$A_{A\,0^\circ\,C.}$	0.99970
$B_{A\,0^\circ\,C.}$	0.000580	$B_{A\,0^\circ\,C.}$	0.000512
$A_{A\,100^\circ.20\,C.}$	1.36626	$A_{A\,100^\circ.35\,C.}$	1.36667
$B_{A\,100^\circ.20\,C.}$	0.000863	$B_{A\,100^\circ.35\,C.}$	0.000673

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1) Comm. Leiden N⁰. 100*b*.

2) Comm. Leiden N⁰. 102*b*.

From these data and with $\alpha_A = 0.0036618$ the corrections to be applied to the Celsiusscales of the international hydrogen- and helium-thermometer in order to reduce these scale onto the Celsius-Avogadroscales of hydrogen and helium, based upon $\alpha_A = 0.0036618$, could be calculated, by means of the relation

$$\triangle_A = t_{A\varkappa} - t_{i\varkappa} = \frac{t_{A\varkappa} \cdot p_0}{A_{A0^\circ \mathrm{C.}} \cdot \alpha_A} \times$$
$$\times \left(\frac{B'_{100}(1+100\alpha_A) - B'_0}{100} - \frac{B'_T(1+\alpha_A\, t_{A\varkappa}) - B'_0}{t_{A\varkappa}} \right) {}^{1)}$$

The temperature-determination will be discussed in detail in the following Communication.

§ 4. *Results of the measurements.*

1. *The temperature of the waterbath.* The readings of the mercury-thermometer P. T. R. N°. 46371, corrected after several determinations of its zero-point, were repeatedly controled with the helium- and hydrogen-thermometer. The results were very satisfactory. Some of them are given in the following table.

Mercury-therm.	Helium-therm.	Hydrogen-therm.
15.531	15.540	—
15.527	15.532	—
12.753	12.755	12.752
12.758	12.764	—

2. *The gasquantities.*

Date	Measurements	H_2
23.1.23	in waterjacket	667.91
29.1.23	at 18°,14 K.	—
„	at 15°,67 K.	—
31.1.23	in waterjacket	667.85
7.2.23	at 90°,23 K.	—
12.2.23	in waterjacket	667.89

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1) Comm. Leiden Suppl. N°. 23 pag. 904. This equation agrees with Suppl. N°. 51*a* equation (25).

Of another filling:

Date	Measurements	H_2	He
17.6.24	in waterjacket	690.29	741.44
19.6.24	at 69°,85 K.	—	—
21.6.24	in waterjacket	690.33	741.43
24.6.24	at 16°,67 K.	—	—
25.6.24	in waterjacket	690.29	741.44
26.6.24	at 14°,54 K.	—	—
8.7.24	in waterjacket	690.28	741.42

Of the interchanged fillings:

Date	Measurements	H_2	He
17.7.24	in waterjacket	686.30	686.19
18.7.24	at 18°,22 K.	—	—
19.7.24	in waterjacket	686.44	686.32

In this case both gasquantities appear to have increased, from which one might conclude to a small leak at each side. This leak, however, should be just as large for the helium-side as for the hydrogen-side. Hence it seems more probable that for one of the two measurements the temperature has been read incorrectly.

3. Values of pv_A.

a. the left side (movable point-tube) is filled with hydrogen, the right side (stationary point-tube) with helium.

For the sake of completeness the results of PALACIOS MARTINEZ and KAMERLINGH ONNES [1]) at the same temperature, recalculated with the same virial-coefficients at 0° C. and 100° C. and using the same expansion of Jena-glass 16^{III} that unterlies all the present results, must be included here.

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[1]) PALACIOS MARTINEZ and KAMERLINGH ONNES, Comm. Leiden N^0. 164.

The results communicated there were calculated for helium with $A_{A0} = 0.99950$ and $B_{A0} = 0.000499$, with the temperature correction for the expansion of glass obtained by extrapolating LINDEMANN's measurements, and so these differ somewhat from those given here.

N^0.	Hydrogen			Helium		
	d_A	pv_A	O.—C.	d_A	vp_A	O.—C.
Measurements at 90°,23 K. 1)						
1	0.71898	0.33011	+ 0.00001			
2	2.11256	0.32991	— 3			
3	3.55674	0.32977	+ 1			
Measurements at 69°,86 K.						
1	0.74379	0.25551	+ 0.00003	0.74310	0.25582	+ 0.00003
2	2.19020	0.25518	— 2	2.2150	0.25591	— 3
3	3.68698	0.25487	— 4	3.7153	0.25607	— 2
4	6.64996	0.25436	+ 3	6.6706	0.25641	+ 2
Measurements at 20°,55 K.						
1	1.32349	0.074561	+ 0.000001	1.32680	0.075229	+ 0.000037
2	6.42783	0.072163	+ 2	6.68009	0.775170	0
3	8.98884	0.070957	0	9.36906	0.075158	— 1
4	11.4336	0.069804	— 4	11.98147	0.075148	0
Measurements at 20°,53 K.						
1	1.33822	0.074449	— 0.000075	1.33583	0.075149	— 0.000001
2	3.84188	0.073332	— 5	3.99821	0.075127	— 1
2*				4.00075	0.075137	+ 9
3	6.4228	0.072124	+ 10	6.70706	0.075094	— 8
4	11.5316	0.069687	— 5	12.0625	0.075056	+ 2
4*	11.5322	0.069678	— 14			
Measurements at 20°,51 K. 2)						
1				1.33622	0.075153	+ 0.000083
2				3.95905	0.075046	+ 0
3				6.62529	0.075024	+ 2
4				11.8983	0.074973	— 1

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1) The helium measurements were discarded as later an impurity was found in the filling.

2) The hydrogen-thermometer was broken at the beginning of the measurements.

Measurements by PALACIOS MARTINEZ and KAMERLINGH ONNES:

N⁰.	Hydrogen			Helium		
	d_A	pv_A	O.—C.	d_A	pv_A	O.—C.
	Measurements at 20°,51 K.					
1	1.32857	0.074442	+ 0.000046	1.28965	0.074987	+ 0.000002
2	3.81226	0.073214	+ 5	3.82072	0.074984	+ 18
2*	3.81205	0.073202	— 7	3.82048	0.074945	— 21
3	6.37529	0.071990	+ 6	6.39307	0.074949	+ 2
4	11.4486	0.069555	— 4	11.48163	0.074906	— 3
	Measurements at 20°,49 K. [1]					
1	1.36628	0.074323	— 0.000005			
2	6.43773	0.071937	+ 3			
3	9.00150	0.070728	+ 4			
4	11.4495	0.069566	— 3			
	Measurements at 20°,49 K. [1]					
1	1.31556	0.074350	+ 0.00004			
2	6.37416	0.071930	— 8			
3	8.93236	0.070725	+ 5			
4	11.4188	0.069538	+ 1			

Here follow again the results of our own measurements.

N⁰.	Hydrogen			Helium		
	d_A	pv_A	O.-C.	d_A	pv_A	O.-C.
	Measurements at 18°,16 K. [2]					
1	0.72114	0.066140	+ 0.000032			
2	2.13567	0.065380	— 5			
3	3.59389	0.064624	— 32			
4	6.48021	0.063202	+ 4			

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[1] On the helium side only the first density was measured.

[2] See note for the measurements at 90°.23 K. (note 1 p. (679).

N^0.	Hydrogen			Helium		
	d_A	pv_A	O.—C.	d_A	pv_A	O.—C.
Measurements at 16°,65 K. 1)						
1	0.74516	0.060743	0.000197	0.74442	0.060897	— 0.000045
2	2.20766	0.059776	0	2.23038	0.060905	0
3	3.71491	0.058982	0	3.73868	0.060868	0
Measurements at 15°,64 K. 2)						
1	0.72123	0.056851				
2	1.33022	0.056514				
Measurements at 14°,50 K. 3)						
1	0.74508	0.052630				
2	1.32974	0.052284				
2*	1.32014	0.052297				

b. Interchanged fillings. The left side (movable point-tube) is filled with helium, the right side (stationary-point-tube) with hydrogen. (See table following page).

Before stating the coefficients calculated from these data, for which the corresponding differences between observed and calculated pv_A's are

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1) If one tries to represent these 3 points by an equation, one finds impossible B-values, and improbable values for O.—C. It seemed better therefore to give little weight to the first density which at these low temperatures is measured with pressures of but a few cm of mercury, and to draw a straight line through the points 2 and 3. The control which would have been given by more points, is lacking in this case.

2) At first we found at 15°,67 K.:

1. 0.721228 0.056829.
2. 2.136585 0.055871.

The very large value for B_A which results from these, renders it probable that there is an error in one of the two measurements. Therefore values for d_A and pv_A were calculated from a measurement of CATH and KAMERLINGH ONNES (Comm. Leiden N^0. 156, table 1*b*) at a somewhat lower temperature, with the differential thermometer filled with helium and hydrogen. Combination of this pv_A with measurement N^0. 1, both reduced to the same temperature, gives a B_A, which is in complete agreement with all the others, whilst N^0. 2 does not give that agreement,

3) A second point is obtained from the measurements of CATH and KAMERLINGH ONNES mentioned in 2). Here two determinations could be used, one at a somewhat lower, the other at a somewhat higher temperature.

N^0.	Helium			Hydrogen		
	d_A	pv_A	O.—C.	d_A	pv_A	O.—C.
Measurements at 18°,22 K.						
1	0.74063	0.066770	+ 0.000099 [1]	0.74035	0.066294	+ 0.000005
2	2.1940	0.066635	+ 1	2.21855	0.065536	— 7
3	3.6909	0.066599	+ 1	3.71861	0.064787	+ 2
4	6.6472	0.066523	0	6.68772	0.063282	— 4
4*	6.6581	0.066526	— 3			

already given in the foregoing tables, we can make the following remarks:

1. The measurements at 20°,50 K. may certainly (see PALACIOS MARTINEZ and KAMERLINGH ONNES) be supposed to have an accuracy for the pv_A's of $^1/_{10000}$. The same is true for the measurements at 70° and 90° K. For the other measurements, at which the zero-pressure was always 500 mM., this accuracy is reached for the normal-volumes, but not for the pv_A's, as here pressures of 2 à 3 cM. of mercury had to be measured. Moreover once or twice abnormal errors appeared, which are seen in the columns O—C, and which are possibly due to the still too narrow tap-openings, which perhaps were filled up with tap-grease, so that with very small pressure differences there was not a free passage.

2. The accuracy of the B-values is seen best from the complete agreement of the results at 20°,53 K. and 20°,55 K. as well as from the agreement with the B's of PALACIOS MARTINEZ and KAMERLINGH ONNES at these temperatures.

Also at 18°,2 K. the measurements with normal and with the interchanged fillings gave the same values.

With the B-values, derived from only two points, one has to be very careful in drawing conclusions, as appears clearly from the measurement at 15°,6 K., but particularly when the two points are not measured isothermly. The B_A's lying on a smooth curve, (see below) inspire confidence.

The smaller B-values at 70° and 90° K. are proportionally less accurate for the greater values pv_A. The same is true for these of helium at 70° K. and more so for the very small B-values in liquid hydrogen. Still we obtain as the average of three determinations at about the same temperature

$$-0.0000072$$

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[1] This point has been discarded for the calculation of B_A.

whilst Palacios Martinez and Kamerlingh Onnes obtained:

$$-0.0000075.$$

3. After the fillings were interchanged, no deviations, but exactly the same results were obtained, so that there is no reason to suppose any asymmetry.

4. The measurements, including those with interchanged fillings confirm the conclusion, which Palacios Martinez and Kamerlingh Onnes drew, concerning the possible presence of quanta-influences in the form of a term $Qd^{2/3}$ in the equation of state. We also find that the measurements do not necessitate the interpolation of such a term in the equation of state.

5. The B-values of Kamerlingh Onnes and de Haas at 20°,6 and 17°,8 K. differ about 2 and 4 % with those, determined here, whilst the value at 16° K. differs completely.

4. *Virial-coefficients of hydrogen.*

At the measured temperatures following coefficients were obtained:

T	A_A	B_A
90°.23 K	0.33019	— 0.0001202
69.86	0.25562	1939
20.55	0.075182	4700
20.53	0.075158	4740
18.16	0.066472	5053
16.65	0.060938	527
15.64	0.057250	5533
14.50	0.053063	581
interchanged fillings:		
18.22	0.066663	5055
From Palacios Martinez and Kamerlingh Onnes:		
20.51	0.075031	— 0.000478
20.49	0.074973	472
20.49	0.074972	476

Fig. 3 represents the B-values obtained, and also the results of Kamerlingh Onnes and Braak [1]) and of Kamerlingh Onnes and de Haas (resp. indicated by □ and △).

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[1]) Comm. Leiden N⁰. 100a.

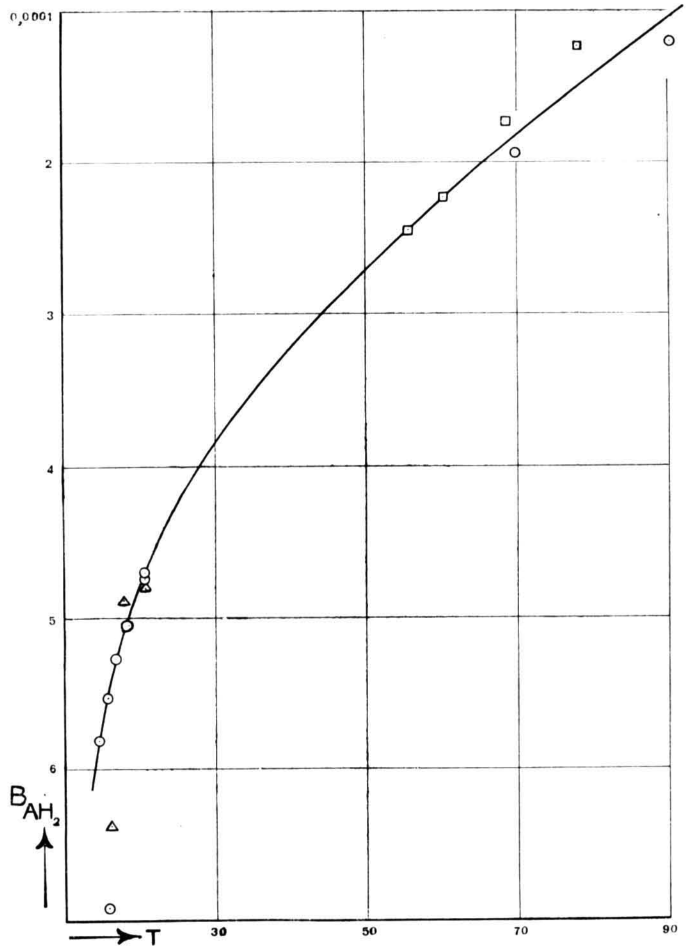

Fig. 3.

From the *B*-values result the following corrections, to be applied to

Corrections of the international hydrogen-thermometer
onto the Celsius-Avogadroscale.
$(\alpha_A - \alpha_{iH_2} = -0{,}000\,0009)$ 1)

T	t	$\Delta_A = t_{A\alpha} - t_{H_2\alpha}$
90.23 K.	— 182.86C	+ 0.067
69.86	203.23	72
20.55	252.54	12 1
20.53	252.56	122
18.16	254.93	131
16.65	256.74	137
15.64	257.45	146
14.50	258.59	155

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1) The numbers given here are somewhat different from those given in Comm. Leiden Suppl. N⁰. 51*a* Table XI, owing to the somewhat changed value of $\alpha_A - \alpha_{iH_2}$.

the temperatures on the Celciusscale of the international hydrogen-thermometer, in order to reduce these temperatures onto the Celsius-Avogadroscale of this gas. (Fig. 4).

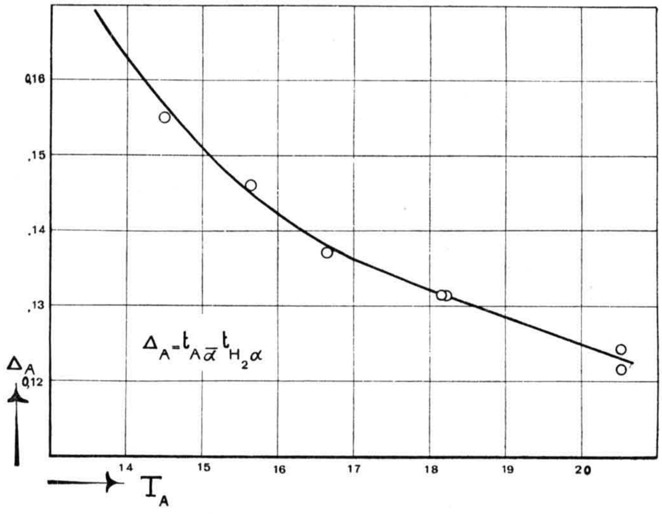

Fig. 4.

5. *Virial-coefficients of helium.*

T	A_A	B_A
69.86	0.25572	+ 0.0001003
20.55	0.075198	— 0.0000042
20.53	0.075162	90
20.51	0.075082	91
18.22	0.066689	244
16.65	0.060960	245
From PALACIOS MARTINEZ and KAMERLINGH ONNES:		
20.51	0.074963	— 0.0000074

We obtain from this graphically the BOYLE-point of helium at 22°,1 K.

From the foregoing results can be calculated the following corrections for the intern. helium-thermometer. (See table following page).

In fig. 5 the results of KAMERLINGH ONNES[1]) are also given, indicated by □.

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[1]) Comm. Leiden N⁰. 102*b*.

Corrections for the international helium-thermometer onto the Celsius-Avogadroscale.

$(\alpha_H - \alpha_{iHe} = 0{,}000\,000\,3^4)$

T	t	$\Delta_A = t_{A\alpha} - t_{H2\alpha}$
69.86 K.	− 203.33C.	+ 0.031
20.55	252.54	41
20.53	252.56	42
20.51	252.58	43
18.22	254.87	46
16.65	256.44	46

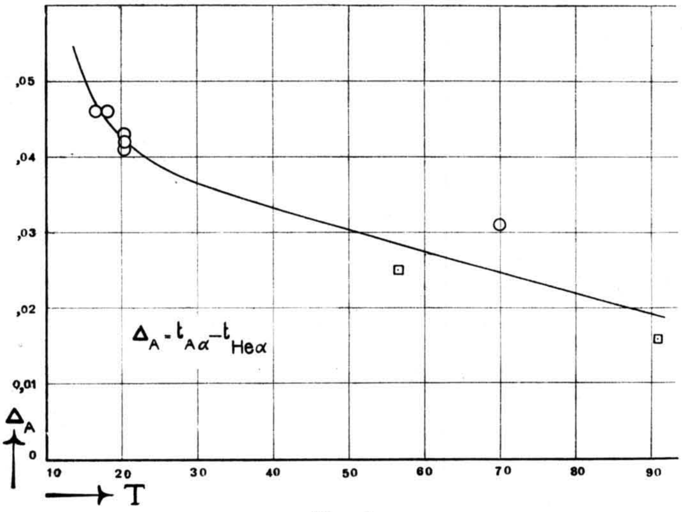

Fig. 5.