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small inclination β and that electric charges exist at the front and at the back of the discharge.

In that case we again find the formula (51), in which v_1 v_2 u_1 and u_2 are given by the formulae

$$\begin{vmatrix}
v_1 &= k_1 X \\
v_2 &= k_2 X \\
u_1 &= k_1^2 H X + k_1 Y \\
u_2 &= k_2^2 H X - k_2 Y
\end{vmatrix}.$$

The place of (52) is taken by the formula

$$tg \beta = \frac{u_2 - u_1}{v_1 + v_2} \cdot \cdot \cdot \cdot \cdot \cdot \cdot (60)$$

From (51) and (60) we conclude

$$U = k_1 k_2 HX \dots \qquad (61)$$

and

$$tg \beta = (k_2 - k_1) H - \frac{Y}{X}$$
 (62)

Whatever the inclination may be, we always find the right value for the velocity U. So it appears reasonable to suppose that this inclination is determined by the local conditions of the metal and that the electric intensity Y and the charges to which it is due, adjust themselves to it according to (62).

Physics. — "The atomic volume of allotropic modifications at very low temperatures." By Prof. Ernst Cohen and Dr. J. Olle Jr. Communication No. 113 from the Physical Laboratory at Leiden. (Communicated by Prof. H. Kamerlingh Onnes).

(Communicated in the Meeting of October 30, 1909).

1. In the discussion on a communication: "The allotropic forms of silver and gold", made by one of us in the meeting of the Deutsche Bunsengesellschaft at Dresden) the question was raised whether the atomic volumes of the different allotropic modifications of a certain element become equal at the absolute zero point. As the answer to this question, which can only be given by experiment, is in the closest connection with some other points concerning the periodic system of the elements to which we shall come back later on, we have carried out an investigation in the above mentioned direction, which may be briefly described here.")

¹⁾ Zeitschrift für Elektrochemie 21, 589 (1906).

²⁾ The full discussion will shortly appear in the Zeitschnift für physik. Chemie

- 2. We have carried out our measurements only with diamond and graphite, and with white and gray tin, as a preliminary-investigation showed us, that the allotropic forms of phosphorus were less suitable.
- 3. Through the kindness of Mr. S. Lemmans of Amsterdam Mr. Louis Tas placed ten grammes of diamond (314 pieces) at our disposal. We may be allowed here also to express our hearty thanks to them.
- 4. Mr. P. Lebeau of Paris sent us a large quantity of graphite, made by the late Henri Moissan; on investigation this preparation appeared to be very pure.

As the researches of Le Chateler and Wologdine 1) have shown that graphite assumes a sharply defined specific gravity at a certain temperature only when it has been exposed to great pressures (according to the above writers enclosed gases are expelled from it in this way), we have exposed our preparation to pressures of 5000—10000 atms., and have not used it until the spec. grav. remained constant after repeated compression.

We made use of an apparatus constructed specially for this purpose, which is reproduced in fig. 1.

In the steel block B a hole is bored, into which powdered graphite is put. In this hole fits the steel piece D, which is pressed down through the block A under an hydraulic press. The graphite cylinder made in this way may be easily removed from B, if C is unscrewed, and may then be pushed from the hole by means of the piece FE.

5. The white tin, which was used in our measurements, was the same preparation that served in the investigations of Ernst Cohen and E. Goldschmut'); the grey tin came from a block of Banka tin, which on a former occasion had been kindly presented to us by Mr. H. Baucke, chemical engineer 3). On investigation this material proved to be very pure. By a special investigation we convinced ourselves that it did not contain any white tin.

DETERMINATION OF THE SPECIFIC GRAVITY.

- 6. Our determinations were carried out at 18° , -38° , and -164° .
 - · A. Measurements at 18".0.
- 7. For this purpose we made use of a pycnometer. As graphite is not moistened by water, we took toluene as filling liquid. In

¹⁾ G. R. 146, 49 (1908).

²⁾ Zeitschrift für physik. Chem. 50, 225 (1905).

³⁾ Zeitschrift für physik. Chem. 63, 625 (1908).

connection with this the ground-glass stopper of the pycnometer was made very long. Our apparatus had a capacity of ± 22 cc.; it was gauged by means of water carefully freed from gases by boiling. The weighings were carried out on a balance, on which $\frac{1}{10}$ mg. could be read. All weighings were reduced to vacuum and to the density of water at $4^{\circ}.0$.

After the substance which was to be examined, had been introduced into the pycnometer, the latter was filled with toluene, and connected with the air pump. When the toluene had boiled for some time, the pycnometer was again filled up with thatliquid, and placed in a thermostat, which was kept at 18°.0. The thermometers used were tested by a normal thermometer (divided into 1/10°), which had been tested by the Physikalisch-Technische Reichsanstalt at Charlottenburg.

The stopper of the pycnometer had a capillary bore; the upper surface of the capillary was made opaque by grinding. As soon as this upper surface remained perfectly dry for ten minutes, the liquid was sucked off by means of a capillary pipette down to a mark on the capillary of the pycnometer. Then the pycnometer was removed from the thermostat, and weighed after having been carefully dried. All the determinations were made twice.

For the toluene used we found: $d = \frac{18^{\circ}.0}{4^{\circ}.0}$ **0,8666**.

Table I contains the results of the determinations at 18°.0.

TABLE 11)
Temperature 18°.0.

Substance		Weight of the	Weight of the	d. 18°.0	D
Name	Weight in gr.	expelled toluene in gr.	expelled water in gr.	a, 40.0	Remarks
Diamond	9.9790*	-	2.8296*	3.514	
Graphite	8.4424*	3.2964*	_	2.217	
Graphite	8.5504*	3.3412*		2.215	
White tin	16.8488	<u>-</u>	2.3082	7.281	prepar. from grey tin
White tin	23 7052*		3.2458*	7.285	" from melted tin
Grey tin	33.4100*	_	5.7953*	5.751	fine powder
Grey tin	29.9170	_	5.1789	5.763	coarser "
			١ ,		1

¹⁾ The values in this table marked with an * have served in the further calculations,

B. Measurements at low temperatures.

8. As far as we know an accurate method of determining the specific gravities 'of solid substances at very low temperatures does not exist yet '), we therefore had in the first place to devise one.

Our method may be considered as a combination of the dilatometer and the weight-thermometer.

It appeared at the outset that we could extend our experiments no further than — 164°. For no liquid is known as yet which remains sufficiently fluid below that temperature. Pentane e.g. (so-called Pentan für Thermometer) becomes so viscous a few degrees lower, that it is of no use whatever.

a. The dilatometer.

9. Our dilatometer (Fig. 2) was made of Jena glass 16^{III}, as the coefficient of expansion of this kind of glass at very low temperature is sufficiently known through the investigations of Kamerlingh Onnes and Clay.

A is a reservoir of a capacity of ± 20 cc.; the capillary BB_1B_2 has a bore of 0,7 mm.; the capacity of C is ± 6 cc., that of $E \pm 20$ cc.

By the aid of a ground-glass junction S, E could be placed on the capillary tube. This has the same bore as BB_1B_2 .

The course of the experiment is now as follows:

After A has been cleaned and weighed, the substance which is to be examined as to its specific gravity, is introduced, and the whole is weighed again. The tube BB_1B_2 is fused on to it and the whole weighed again. Then a mark is etched on the capillary BB_1B_2 , just below the place where the level of the cooling liquid will ultimately be. A is filled with pentane up to this mark, after it has been brought to $18^{\circ}.0$ in a thermostat. It is weighed again.

Now A is put into a refrigerating mixture, and the other part of the apparatus is fused to the capillary at B_z .

E is connected with a three-way tap (not greased), which enables us to exhaust the apparatus, and to fill it up with pentane. These manipulations are repeated a few times.

If in this way the apparatus has been filled with pentane to about halfway the height of E, we pour pure, doubly distilled mercury

¹⁾ The determinations made by Dewar, Chemical News 85, 289 (1902), were of a more preliminary character. His method was altogether unsuitable for our purpose as it is not sufficiently accurate.

Prof. ERNST COHEN and Dr. J. OLIE Jr. "The atomic volume of allotropic modifications at very low temperatures-"

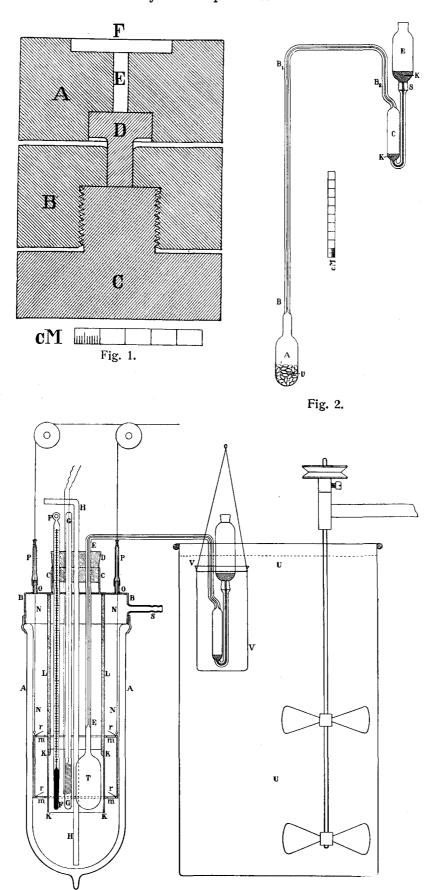


Fig. 3.
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into E by means of a funnel. We remove the excess of pentane by-exhausting once more, so that the mercury at last penetrates into the bottom part of C, and KS remains filled with it.

ABB, is placed in the cryostat, and B_2CSE in a thermostat U (fig. 3), which is kept at 18°.0.

The mercury now rises in C; mercury is poured into E, so that, when A has assumed the temperature of the cryostat, the mercury in E stands a few centimeters above the ground-glass junction.

If the temperature of the cryostat has remained perfectly constant for an hour (the temperature is determined by means of a resistance thermometer), E is removed. The excess of mercury in E, is then received in a glass beaker V (fig. 3). If the capillary remains quite filled to the top, the vessel E is again placed on the ground-glass junction after having been care fully cleaned beforehand, and now the temperature of ABB_1 is slowly raised. The mercury that issues at S, is received in E. After some time the whole apparatus is placed in the thermostat of $18^{\circ}.0$, and there it is left for a considerable time. Now a glass beaker is placed under B_1CSE , E is carefully removed from the ground-glass junction, so that the mercury flows into the beaker, the mercury on the surface of the ground junction being collected with a feather.

The mercury found in the beaker is carefully washed with water, then with alcohol. This is removed by means of a current of air which has been filtered through cotton wool. The drying is repeated, till the weight has become constant.

b. The Cryostat.

10. For the measurements at -38° we used liquid methyl chloride under reduced pressure, at -164° liquid methane at 1 atm. The apparatus constructed by Kamerlingh Onnes for such purposes 1), is diagrammatically represented in fig. 3. AA is an entirely transparent vacuum glass, which can contain \pm 2 liters of liquid, BB is a brass cover, which can be fastened gastight on the glass by means of a rubber ring. The neck CC can be closed gastight by means of a large rubber stopper. The stopper D was pierced in six places; through three holes passed the capillaries E of three dilatometers. Moreover the glass vessel AA was provided with a resistance thermometer G, a pentane thermometer F, and a glass tube H. The last reached to the bottom of the vacuum glass.

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¹⁾ These Proc. June 1905; Comm. from the Phys. Lab. at Leyden No. 94c.

The reservoirs T of the dilatometers were surrounded by a protecting jacket KKKK of nickel plate. This jacket was supported by the nickel bars LL. The liquid gas was kept in violent motion by the stirrer mm. The valves rrrr promote the stirring in a high degree. The stirrer is suspended on three wires NN, which pass airtight through the cover BB. To satisfy this condition they pass through the metal tubes OO, and through the rubber tubes PP; in the latter the wires are fastened airtight. By means of an electromotor the wires are brought in an upward and downward motion.

The liquid gas was pumped into the vacuum glass by means of the tube HH.

When we worked under reduced pressure, S was connected with the airpump.

11. The tables 2-9 contain the results of the measurements, which are used in the calculation.

TABLE 2
Temperature 18.00.

The dilatometer contains	Weight of the solid substance in gr.		Number of the dilatometer
Diamond—Pentane	9.9790	12.0820	I
Graphite—Pentane	8.7954	11.6135	II
White tin-Pentane	23.7026	12.7496	III ·
Grey tin-Pentane	26.4843	10.5339	IV
Pentane		12.8847	V
Water	_	20.2058	, v
i	- 1		}

TABLE 3.
Temperature —163°.6.

Number of the dilatometer	The dilatometer contains	Weight in gr. of the mercury that has flowed out at 18°.0.
I	Diamond – Pentane	67.5817
II	Graphite—Pentane	65.0153
V	Pentane	72.1680

(443)

TABLE 4. Temperature — 163°.2.

Number of the dilatometer	The dilatometer contains	Weight in gr. of the mercury that has flowed out at 18°.0	
I	Diamond—Pentane	67.6155	
. II	Graphite—Pentane	65.0644	
V	Pentane	72.2079	
	TABLE 5. Temperature — 163°.5.		
Number of the dilatometer	The dilatometer contains	Weight in gr. of the mercury that has flowed out at 18°.0	
I	Diamond – Pentane	67.5664	
II	Graphite—Pentane	′ 65.0778	
V	Pentane	72.2685	
	TABLE 6. Temperature — 38°.0.		
Number of the dilatometer	The dilatometer contains	Weight in gr. of the mercury that has flowed out at 18°.0	
I	Diamond—Pentane	21.2138	
Ĭ	Graphite—Pentane	20.4593	
v	Pentane	22.7002	
	TABLE 7. Temperature — 37°.75.		
Number of the dilatometer	The dilatometer contains	Weight in gr. of the mercury that has flowed out at 18°.0	
I	Diamond—Pentane	21.1658	
II	Graphite—Pentane	20.3958	
` v	Pentane	22.6509	
	TABLE 8. Temperature — 163°.3.		
Number of the dilatometer	The dilatometer contains	Weight in gr. of the mercury that has flowed out at 18°.0	
III	White tin—Pentane	74.7480	
IV	Grey tin-Pentane	58.9882	
V '	Pentane	72.2378 30*	
		1	

TABLE 9. Temperature — 163°.4.

Number of the dilatometer	The dilatometer contains	Weight in gr. of the mercury that has flowed out at 18°.0
III	White tin—Pentane	74.7131
IV	Grey tin-Pentane	58 9744
V	Pentane	72.2318

12. The calculation of the experiments may be summarized here as follows: if we call:

 P_d the weight of the diamond used;

 $P_{18^{\circ},0}^{Ip}$ the weight of the pentane at 18°.0 in the dilatometer I with the diamond;

 $P_{18^{\circ}.0}^{V}$ the weight of the pentane, in the dilatometer V at 18°.0;

 U_p the weight of the mercury which has flowed out during the heating of dilatometer V (filled with pentane) from — t° to 18°.0;

 $S_{18^{\circ}0}$ the specific gravity of mercury at $18^{\circ}.0$;

 $W^d_{18^{\circ}.0}$ the weight of the water that is expelled by the diamond at 18.°0.

 D^{w}_{18} , the density of water at 18.°0;

 σ the mean coefficient of expansion of the (Jena) glass used from 18° to — t° .

 U_d the weight of the mercury which has flowed from dilatometer I, when it is heated from — t° to 18°.0, then the specific gravity of diamond at — t° is

$$S_{-t^{\circ}} = \frac{P_d}{P_{18^{\circ},0}^{\text{I}_p} \frac{U_p}{P_{18^{\circ},0}^{\text{V}}} + \frac{W_{18^{\circ},0}^d}{D_{18^{\circ},0}^w} (1 - \sigma(t + 18^{\circ})) - \frac{U_d}{S_{18^{\circ},0}}}$$

Table 10 has been calculated by means of this expression (resp. by means of the analogous expressions for the other substances investigated.

(445)

T A B L E - 10.

Temperature	Spec. gravity $d\frac{t}{4^{\circ}.0}$			
ť	Diamond	Graphite	White tin	Grey tin
— 163°.6	3.519	2.223		
163°.2	3.518	2 224		
163°.5	3:509	2.222		
163°.3			7.350	5.768
163°.3			7.354	5.768
— 38°.0	3.510	2.217		
37º 75	3.510	2.217	,	
+ 18°.0	3.514	2.216	7,285	5.751

13. Finally table 11 gives a survey of the ratio of the spec. gravities of different allotropic forms of the same element at different temperatures:

TABLE 11.

Temperature	Ratio $\frac{S_{\text{diamond}}}{S_{\text{graphite}}}$	Ratio $\frac{S_{\text{white tim}}}{S_{\text{grey tin}}}$
+ 18°.0	1.585	1.266
— 38°	1.583	
— 164°	1 582	1.274

14. We see from table 11 that down to -164° there are no indications that the spec. gravities (resp. the spec. volumes) of the different allotropic modifications of the same element converge to one and the same value in approaching the absolute zero point.

It is only owing to the great kindness of Prof. Kamerlingh Onnes, who placed the resources of his laboratory at our disposal, that it has been possible for us to carry out the above investigation. We may be allowed also here to express our great indebtedness to him.

To Mr. G. J. Flim, technical assistant at the Cryogenic Laboratory at Leiden, many thanks are due for his intelligent assistance.

October 1909.