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sides with the same intensity, and when the illumination is then continued on one side, results are obtained completely analogous to those with omnilateral instead of bilateral fore-illumination. It need cause no surprise, that with a *bilateral* illumination, the excess which must be given on one of the sides, to obtain an ipsilateral curvature, inust be greater, in proportion as the tendency to curvature on the other side is stronger. This is the same phenomenon, which we have observed after an *omnilateral* fore-illumination. The quantity of energy, which had to be given in one direction, in order to obtain a positive curvature, was greater in proportion as the previous illumination was more intense.

There is no reason to regard this so-called smaller sensitiveness of a previously illuminated plant, which only depends on the necessity of overcoming a tendency to curve, as an adjustment phenomenon. Rather should this name be reserved for the process which we have here always called adjustment process. We have been able to observe how it is affected both by unilateral and by omnilateral illumination.

Bilateral illumination can also give some explanation of the fading phenomenon (§ 5).

We saw that, as the intervals between the two opposite illuminations become longer, the curvatures show better. This gives us a new point of view with regard to the fading process, which the omnilateral illumination enabled us to study.

Here, with the time which elapses between the first stimulation (omnilateral fore-illumination) and the second one (unilateral afterillumination), the power of the latter of becoming visible increases. This manifests itself in the phenomenon that, the longer the interval has lasted, the smaller is the amount of energy required to produce a visible curvature. We must therefore assume that the gradual return of the original sensitiveness is the result of the fact that a tendency to curvature can express itself more strongly when a longer period has elapsed since the last stimulation.

## Utrecht, Botanical Laboratory.

## Chemistry. — "The Allotropy of Copper" I. By Prof. ERNST COHEN and Mr. W. D. HELDERMAN.

1. In studying the earlier literature on copper we found certain indications which justified the presumption that this metal is capable of existing in different allotropic modifications. This presumption had been strengthened by the results of our investigations on tin, bismuth, cadmium and zinc. We will discuss the indications referred to above in our detailed paper in the Zeitschrift fur physikalische Chemie; here only two points may be specially mentioned: 1. MATTHIESEN and von BOSE<sup>1</sup>) found as early as fifty years ago, that wires of electrolytic copper had changed their electric conductivity (at 0° C.) after having been heated for some time at 100° C. Table 1 illustrates this phenomenon.

Wire 1 at 0°	Wire 2 at 0 <sup>0</sup>	Wire 3 at 0º
99.526	100.021	100.327
99.943	99.971	100.461
101.097	100.268	100.563
101.418	100.524	100.645
101.671	100.656	100.708
101.682	101.075	100.649
'	101.230	100.705
	101.469	
	Wire 1 at 0° 99.526 99.943 101.097 101.418 101.671 101.682	Wire 1 Wire 2   at 0° at 0°   99.526 100.021   99.943 99.971   101.097 100.268   101.418 100.524   101.671 100.656   101.682 101.075    101.230    101.469

TABLE I.

2. Even in those cases where pure copper was used, the values given in the literature for the density of this metal differ amongst themselves very considerably.  $^{1}$ )

2. "We carried out our experiments in the same way as those described in our paper "On the Allotropy of Zinc". <sup>2</sup>)

Electrolytic copper (KAHLBAUM — Berlin, "geraspelt") was brought in quantities of 100 grams each into a porcelain crucible. The pure metal was melted in an electric furnace, some charcoal powder having been added to it. The melted material which showed a brilliant surface was poured out into cylinders made of asbestos-paper. As soon as the metal had solidified, the cylinders were chilled in water and turned into thin shavings on a lathe.

55 grams of this material after having been washed with ether, dilute nitric acid, water, alcohol, ether, and dried in vacuo over sulphuric acid, were put into a pycnometer in order to determine the density at  $25^{\circ}$  C. We then observed that the water meniscus in

<sup>1</sup>) POGGENDORFF'S Ann. 115, 353 (1862).

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<sup>1</sup>) Compute e g KAHLBAUM II. SIULM, Zeitschr. f. anorg. Chemie **46**, 280 (1905) <sup>2</sup>) Proceedings **16**, 565 (1918).

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the pycnometer was continually falling at constant temperature. The same phenomenon was observed when the experiment was repeated. This indicates that the metal undergoes some change at this temperature.

3. By manipulating very quickly we succeeded in determining the density at 25<sup>°</sup>.0 We found in two independent experiments:

 $d \frac{25^{\circ}.0}{4^{\circ}} 8.889$  and 8.890.

Our thermometers had been compared with a standard of the Phys. Techn. Reichsanstalt at Charlottenburg-Berlin.

After having heated the metal during 24 hours at  $100^{\circ}$  in a solution of coppersulphate no change of density was observed. Repeating this experiment at  $25^{\circ}$ , we found

$$d\frac{25^{\circ}.0}{4^{\circ}}$$
 8.899 and 8 900

These experiments prove that there is a transition temperature between  $25^{\circ}$  and  $100^{\circ}$  C.

4. In order to fix this temperature more closely we carried out a determination with the dilatometer, using 300 grams of our chilled metal. The dilatometer (bore of the capillary tube 1 mm.) was filled with paraffinoil, which had been heated for some hours in contact with finely divided copper, until there was no more evolution of gasbubbles.

The dilatometer was now kept at different, but constant temperatures.

Temperature	Duration of measurements in hours	Rise of level	Rise of level in mm per hour
25°.0	0.5	- 545	- 1090
45.0	0.2	— 100	- 500
69.6	0.3	- 148	- 444
71.5	18	- 53	- 3
72.0	4	+ 10	+ 2.5
72.5	11	+ 45	+ 4
73.0	0.5	+ 6	+ 12
75.7	0.4	+ 14	+ 36
80.9	0.4	+ 30	+ 75

TABLE II.

We used the electrically heated thermostat, mentioned in our paper on the allotropy of cadmium  $^{1}$ ).

The results are given in Table 2. (Zie p. 630).

5. This table shows that there is a transition point at  $71^{\circ}.7$  C. From this we conclude that there exist two allotropic (enantiotropic) modifications of copper. The phenomena may be described by the equation:

$$Cu(\alpha) \stackrel{71^{\circ}.7}{\rightleftarrows} Cu(\beta)$$

6. It may be pointed out that the change in the dilatometer has taken place with great velocity notwithstanding the fact that the copper used in this experiment had not been in contact with a solution of coppersulphate. On the other hand there was a large quantity of finely divided metal present. Here, as in the case of bismuth, tin etc, the presence of this powder suffices to accelerate the transitionvelocity very strongly.

7. The following experiment proves that the velocity of the reaction  $\beta$ -copper  $\rightarrow \alpha$ -copper decreases enormously when this powder is not present.

We took 200 grams of electrolytic copper, melted it in an electric furnace and poured the metal into a melting-spoon, where a series of thin rods was formed. These rods were chilled in water and put into a dilatometer which was filled with paraffinoil. The apparatus was kept during 14 days and nights in a thermostat at 25° C. Practically no change occurred. The transition velocity of  $\beta$ -copper nto  $\alpha$ -copper is several thousand times smaller than if the finely livided metal is present.

This phenomenon explains the fact that objects made of copper lisintegrate so slowly in daily life. It is exactly the retardation observed in the experiment described above, which makes possible the use of copper in daily life. We meet here with the same observed already in the case of tin, pismuth, cadmium and zinc.

8. Our experiments prove that we have to consider copper as a *netastable* system  $(a + \beta \text{ copper})$ , which (below 71°.7 C.) is continuously changing into the stable modification (*a*-copper). The very trongly marked retardations have concealed the allotropic change from the physicists and chemists who have studied this metal in lifterent directions.

9. Dr. CH. M. VAN DEVENTER has been so kind as to call our

<sup>1</sup>) Proceedings 16, 485 (1913).

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10. The properties of copper  $\alpha$  and  $\beta$  as well as some problems relating to the technical use of copper will be discussed shortly.

VAN 'T HOFF-Laboratory.

Utrecht, December 1913.

## Chemistry. — "The metastability of the metals-in consequence of allotropy and its significance for Chemistry, Physics and Technics." By Prof. ERNST COHEN.

1. The research which I have carried out during these last few months in collaboration with A. L. TH. MOESVELD and W. D. HELDERMAN, has proved that several metals which until now were only known in one modification are capable of existing in two (or more) allotropic forms. The continuation of these investigations will show if all metals have this property, but we may even already conjecture that this will be the case. A great many observations described in the earlier literature afford evidence in this direction.

2. We were also able to state the fact that the pure metals as we have known them until now are *metastable* systems consisting of two (or more) allotropic forms. This is a consequence of the very strongly marked retardation which accompanies the reversible change of these allotropic modifications both below and above their transitionpoints. Employing certain devices (using the metals in a very finely divided state, adding an electrolyte) it is possible to increase the transition-velocity in such a degree, that the change of the metastable to the stable form occurs within a short time.

As such changes are very often accompanied by marked changes of volume, the material is generally disintegrated.

3. As until now, chemists and physicists have always dealt with the  $\alpha$ - and  $\beta$ -form together, all the physical constants of metals, which have been determined, refer to the complicated metastable systems. These are entirely undefined as the quantities of the  $\alpha$ - and  $\beta$ -modifications they contain are not known.

Now it is known that a special physical property of any substance at a definite temperature and pressure depends on its allotropic