Chemistry. — *"The allotropy of zinc."* I. By Prof. ERNST COHEN and W. D. HELDERMAN.

As long as half a century ago various investigators tried to solve the problem whether zinc might be capable of existing in different allotropic modifications.[1]) As late as 1890 LE CHATELIER[2]) proved that this metal does really show a transitionpoint in the neighbourhood of 350°. MÖNKEMEYER[3]) found this point at 321°, BENEDICKS[4]) at 330° (melting point of pure zinc 419°.4) whilst the measurements of MAX WERNER[5]) (who found 300°), published some weeks ago, agree sufficiently with those of LE CHATELIER. We shall discuss in a subsequent paper the differences which exist amongst the results of the investigators mentioned above. Whilst BENEDICKS mentions a second transitionpoint (at 170°), MAX WERNER was unable to find this point. The question whether it really exists or not may be left open for the moment.

As long ago as 1806 CHARLES HOBSON and CHARLES SYLVESTER[6]) stated that the mechanical properties of zinc are very different in different ranges of temperature. It may be pointed out here (as also stated by ourselves) that zinc which is hard at ordinary temperatures, becomes extremely brittle after having been melted and chilled.

Most of those who have studied this metal, point out that the values which are given in the literature for its density differ amongst themselves very considerably.

This fact has formed the starting point for the researches of KAHLBAUM and his collaborators[7]) (following a way indicated by SPRING) on the influence of very high pressures on the density of metals in general. We shall discuss this question in a special paper; here it may be pointed out that years ago BOLLEY[8]) as well as RAMMELSBERG[9]) carried out some experiments in order to find out

[1]) The earlier literature on this subject will be given in our paper in the Zeitschrift für physik. Chemie.

[2]) C. R. **111**, 414, 454 (1890). Contribution à l'étude des alliages, Paris 1901, p. 416.

[3]) Zeitschr. f. anorg. Chemie, **43**, 182 (1905).

[4]) Arkiv för Matematik, Astronomi och Fysik, 6 (1910), quotation from a separate copy Metallurgie, **7**, 531 (1910).

[5]) Zeitschr. f. anorg. Chem. **83**, 275 (1913).

[6]) NICHOLSON's Journal of Natural Philosophy, **11**,304 (1806). Translation in GEHLEN's Neues allgemeines Journal der Chemie, **6**, 728 (1806).

[7]) Zeitschr. f. anorg. Chemie **29**, 177 (1902).

[8]) LIEBIG's Annalen, **95**, 294 (1885).

[9]) Monatsberichte der königl. preussischen Akad. der Wiss. zu Berlin, 1880, pag. 225.

if its previous history (chilling, slowly cooling etc.) had any influence on the density of zinc. These investigations are not exact enough to yield a definite conclusion. RAMMELSBERG, summing up his measurements, says: "Nach dem Gesagten handelt es sich hier nicht um molekulare Modifikationen. Wir finden nur, dass der schnelle Uebergang aus dem flüssigen in den festen Zustand die Sprödigkeit des Metalls erhöht . . ." It will be proved here that this conclusion does not agree with the facts.

We thought it necessary to carry out fresh experiments on this subject. Considering the results of our investigations on tin, bismuth [1]) and cadmium [2]), and in view of the existence of a transitionpoint at 350° it might be expected that the metal, which has been called "zinc" until now, might be a *metastable* system, containing two or more allotropic modifications of this metal.

The following experiments prove that such is really the case. We melted one kilo of the metal (Zink-"KAHLBAUM"; we were not able to detect any impurity in 100 grams of the material). It was then poured out into a cylinder made of asbestos-paper, which was placed in a glass beaker. The beaker was filled up with solid carbon-dioxyde and alcohol. In this way the melted metal was chilled very quickly. The cylinder of zinc formed in this way, was turned into small pieces on a lathe; the outer layer was not used in the following experiments. The metal was washed with ether; after this we carefully determined its density $\left(d \frac{25°.0}{4°} \right)$, using a pycnometer containing 25 cc. The material was divided into two parts (Zn_I and Zn_{II}), which were manipulated separately.

In this way we found (21 hours after having chilled the metal)

$$d \frac{25°.0}{4°} \quad Zn_I \; 7.130 \quad Zn_{II} \; 7.129.$$

We then brought the samples (weighing each 35 grams) into a Jena glass flask, into which was poured so much of a solution of zincsulphate, (saturated at 15°) that the metal was covered by the solution. The whole was then heated at 100° for a long time.

At different intervals of time we took the metal out of the flasks washed it with dilute hydrochloric acid, and water (until the reactions for SO_4 and Cl had disappeared), alcohol and ether. It was then dried in vacuo, using sulphuric acid as a drying agent. After these operations the density of the two samples was determined again, using the whole mass (35 grams) in the pycnometer.

[1]) Zeitschr. für physik Chemie **85**, 419 (1913).

[2]) Proceedings **16**, 485 (1913).

In this way we found:

Density $d.\frac{25°.0}{4°.}$

	Specimen Zn_I	Specimen Zn_{II}
After	24 hours 7.124	7.128
„	72 „ 7.114	7.121
„	192 „ 7.116	7.112
„	336 „ 7.102	7.109

In comparing these values with the original one, it will be seen that the density has decreased at least 24 units of the third decimal place and that this decrease was a continuous one during the whole experiment.

Now there exists full agreement between these results and that of KAHLBAUM and his collaborators, described in the paper mentioned above. In the distillation of zinc in a porcelain tube in vacuo they determined the place where the metal was deposited in the inner side of the tube by photographing it by means of RÖNTGEN-rays. In this way they found (the photo is reproduced in their paper), that the zinc was deposited at a small distance from the hottest part of the tube. Consequently the metal has been able to remain during the cooling in the condition which corresponded to its temperature. In full agreement with this manner of cooling the density of the metal was found to be very low $\left(d.\frac{20°}{4°}\ 6.922\right)$. This value probably lies very near to the density of pure α-zinc.

Our experiments prove that we have to consider "zinc" as a *metastable* system. The modification formed at high temperatures, only very slowly changes into that which is the stable one at 100° (at ordinary temperature). In this way we find (as in the case of tin, bismuth and cadmium), that our "zinc world" is in a *metastable* condition.

As there exists a great difference between the specific volume of the modifications of zinc, all objects made from this metal will disintegrate in the long run.

In conclusion the following facts may be pointed out:

Quite recently M. U. SCHOOP invented a method of covering any object with a layer of metal. In order to do so (the operation is called "schopieren") the metal (in the form of a wire) is mechanically moved through an oxy-hydrogen flame. A strong current of nitrogen "atomizes" the metal which immediately covers the object which is held before the burner. Evidently this device forms an

ideal method for producing chilled metal. If any object has been covered in this way with "zinc", this layer is in a *metastable* condition after cooling to ordinary temperature.

In consequence such a layer will disintegrate in the long run. That the metal made in this way is not in the ordinary condition is proved by experience. NELBURGER [1]) says about it (in the case of tin):

"....ebenso erleiden diese unter Umständen auch eine teilweise Veränderung ihrer physikalischen Eigenschaften, die in einer Vergrösserung der Härte besteht. .... Während gegossenes Zinn nach der BRINELLSCHEN Kugeldruckprobe einen Härtegrad von 9.5 aufweist, zeigt gespritztes einen solchen von 14.2".

We hope to be able to report shortly on the metastability of these "atomized" metals.

VAN 'T HOFF—*Laboratory.*

Utrecht, November 1913.

Physics. — "*A rapid Thermopile.*" By Dr. W. J. H. MOLL. (Communicated by Prof. W. H. JULIUS.)

Among the many instruments, which have been devised for the quantitative investigation of visible and invisible radiation, the thermopile occupies the foremost place in order of both priority and merit. Though for special researches and under particular circumstances the bolometer and the radiometer may be deemed more suitable, the thermopile has never ceased to find its application, for the most delicate measurement as well as for the simple demonstrative experiment.

It is particularly of late years, that it has once again attracted the attention of a number of investigators, and that numerous improvements in its construction have been tried. All of these had the same purpose, namely to increase the *sensitiveness* of the instrument.

Another property, however, is by no means of less importance, viz. the *rapidity* with which, after the radiation has been admitted or intercepted, thermal equilibrium is reached in the pile. The greater this rapidity, the better is the instrument adapted to the investigation of all sorts of radiation-phenomena of short duration and of rapid variability, and also to those researches which require a long series of successive readings, and which with a slow instrument

[1]) Die Naturwissenschaften, 1, 465 (1913).