Chemistry. — "*On the Enantiotropy of Tin* (II)." By Dr. ERNST COHEN and Dr. C. VAN EYK. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read in the meeting of September 30th 1899.)

1. Continuing our researches on grey (stable) and white (metastable) tin [1]) we first attacked the question of the velocity of change of the white into the grey modification.

According to our first communication the velocity is zero at + 20° C, the transition point.

In the course of our experiments we had received the impression that the change white tin → grey tin, took place more slowly at — 83° than at somewhat higher temperatures.

Such a phenomenon recalls the solidification of super-cooled fused substances where the rate of crystallisation increases as the temperature falls below the melting point until a maximum is reached after which it decreases again [2]).

2. A dilatometer, of 2 cc. capacity, was filled with grey tin which had already repeatedly undergone transformation in both directions. By warming the dilatometer for a few moments to 50° a part of the contents was converted into white tin. The dilatometer was then filled with a solution of pink-salt in alcohol, in order to avoid complications which might arise from crystallisation of the salt at very low temperatures.

The dilatometer was then placed successively in different baths at constant temperatures.

Since the conversion of white tin into grey tin is accompanied by a considerable increase of volume the rise (per minute) of the liquid in the capillary of the dilatometer is a measure of the velocity of transformation. It is necessary, of course, to take care that the quantity of white tin undergoing change remains constant during the whole course of the experiments. For this reason the capillary tube of the dilatometer was made very narrow; the conversion of a very small quantity of white tin then gives a sufficient rise. One mm. of the capillary = 0,00028 cc. Taking the specific gravity of white as 7.3, and that of grey tin as 5.8 the transformation of 8 mgrm. of white tin into the grey modification gives a rise of 1 mm. In this way the following results were obtained.

[1]) These Proceedings, June 24 1899.

[2]) Compare GERNEZ, Journal de Physique (2) 4. (1885) p. 349.
TAMMANN, Zeitschr. fur phys. Chemie 23, 326 (1888).
COHEN, These Proceedings, February 25 1899.

Temperature —83° (Paste of solid carbonic anhydride and alcohol).

Time in minutes	Height of the level of the liquid in the dilatometer (in mm.)	$\frac{\Delta h}{\Delta t}$	
0	100.2		
		2.3	
1	102.5		
		2.5	
2	105 0		
		2.5	
3	107.5		Mean rise
		2.5	
4	110.0		
		2.5	per minute
5	112.5		
		2.5	
6	115.0		2.5 mm.
		2.6	
8	120.2		
		2.8	
9	123.0		
		2.7	
10	125.7		

Temperature —48°.

0	44.0		
		5.0	
1	249.0		
		4.5	
2	253.5		Mean rise
		4.5	
3	258.0		
		5.0	per minute
4	263.0		
		4.0	
5	267.0		4.5 mm.
		4.0	
6	271.0		
		4.0	
8	279.0		

Temperature —15° (Cryohydrate of NH_4Cl)

0	232		
		0.40	
3	233.2		
		0.45	Mean rise
7	235.0		
		0.44	
12	237.2		per minute
		0.43	
15	238.5		
		0.50	0.4 m.m.
24	243.0		
		0.33	
30	245.0		

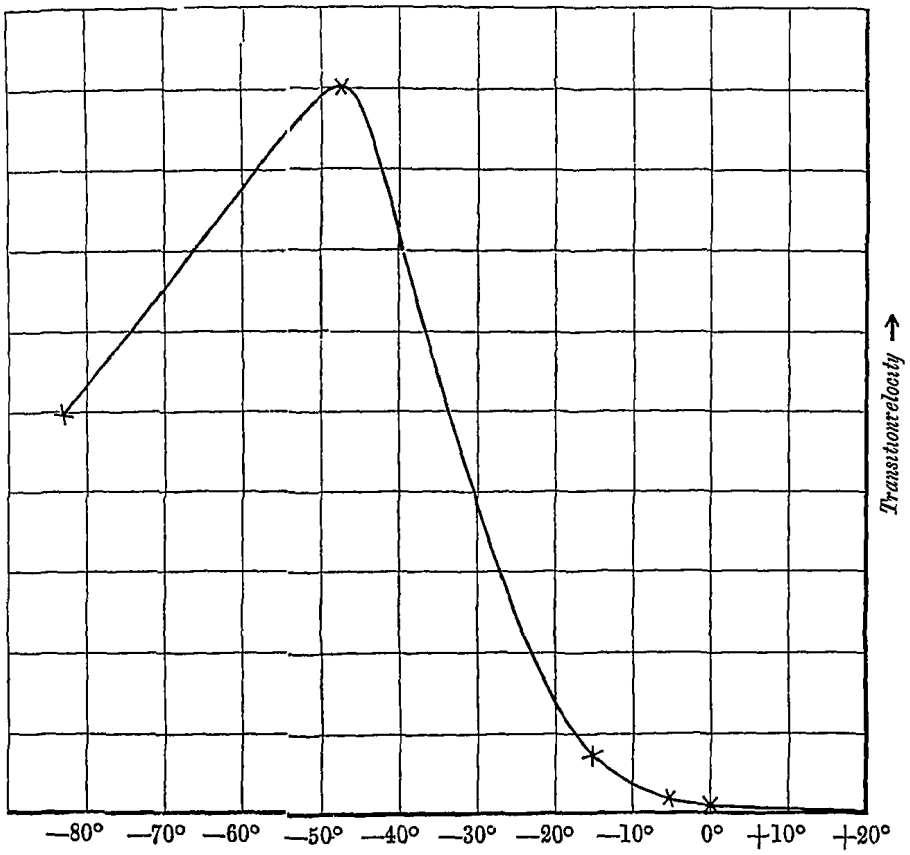
Temperature —5° (Cryohydrate of $MgSO_4$).

0	82		Mean rise
		0.07	per minute
1200	167		0.07 mm.

Temperature 0°.

0	186		Mean rise
		0.03	per minute
1230	234		0.04 m m.

The curve in the figure is obtained by means of these data, the velocities of transformation being taken as ordinates and the temperatures as abscissae.



This curve shows precisely the same course as that above mentioned. There is a maximum at about — 48°; this agrees well with the fact that we had received the impression that the change took place more slowly at — 83° than at a somewhat higher temperature.

If it is desired to convert common white tin into the grey modification a temperature should therefore be selected for the conversion, lying not far from — 48°.

3. So far our experiments had been made with grey tin received from Prof. HJELT of Helsingfors. This was Banca tin which had fallen to powder in a tin store in Helsingfors. The question arose whether the transformation was completely mastered, whether it would be possible to convert any piece of white tin completely into the grey modification.

Our researches in this direction have been crowned with success. We would here express our thanks to Mr. W. HOVY of Amsterdam, who permitted us to make use of one of the so called "evaporators"

in his brewery; this is a reservoir through which a current of brine passes without interruption the temperature of which during our experiments varied between — 7° C. and — 4° C.

The result of the experiments is briefly as follows: (The tin employed was part of a block of Banca tin belonging to the collection of the laboratory).

a. Quite dry, white tin, in the form of a block, was converted into grey tin at the temperature mentioned. The process takes place slowly and begins at the edges.

b. Quite dry white tin, in the form of a block, in contact with traces of powdered grey tin, undergoes change more rapidly. The change begins at the places where the white tin is in contact with the grey tin.

c. White tin in the form of a block immersed in a solution of pink salt undergoes more rapid change than the combination *b.*

d. White block tin, immersed in a solution of pink salt and also in contact with traces of grey tin, is transformed more rapidly than *c.*

e. When the white tin is exposed to the low temperature in the form of filings the process takes place much more rapidly than when the tin is in coherent lumps. The velocities of change under the circumstances mentioned under *a*, *b*, *c* and *d* retain the same order as before.

4. Grey tin, therefore, behaves under all circumstances as if it was infectious. If the change is once started it goes on at higher temperatures (up to 20° C.). *It is thus necessary in these investigations to exercise caution and to take care that traces of grey tin are not imported into tin stores, where their presence might, as it were, give rise to a tin plague.* Grey tin and the finely divided white tin formed from it above 20° C. can hardly be fused together to a coherent mass, a part becoming useless owing to the violent oxidation which it undergoes in the finely divided state.

5. We have already converted large quantities of white tin into the grey modification. In order to attain this result quickly, 500 grams of tin filings were divided between several bottles and some grams of grey tin, which we possessed at the time, were added to the contents of each bottle. The solution of pink salt was also used in the transformation. At — 5° C. a hundred grams of grey tin were obtained in this way in eight days.

6. The destruction of the white tin due to the formation of the

grey modification is enormous. One of our tin blocks is entirely fissured and eaten away on the lower side whilst on the upper surface a number of grey protuberances are visible which gradually become greater finally developing into large cracks.

We shall shortly report on some physical constants of grey tin and on its crystalline form.

We shall be pleased to send a sample of grey tin to any one interested in the matter.

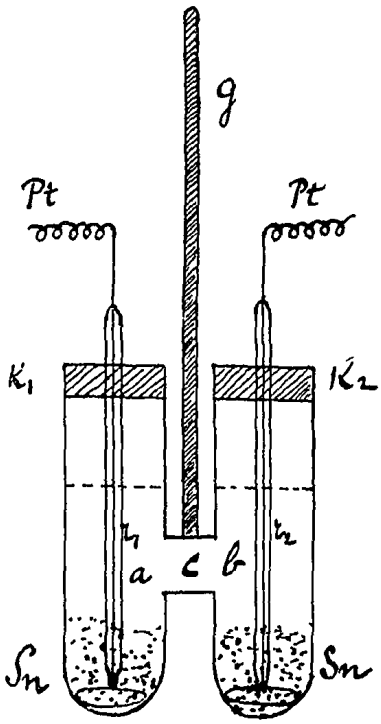
Amsterdam, Chemical Laboratory of the University,
September 1899.

Chemistry. — "*On a new kind of Transition Elements (sixth kind).*" By Dr. ERNST COHEN. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read in the next meeting of September 30th 1899.)

1. The name, sixth kind of transition element, will be applied to elements built up in accordance with the formula:

Electrode of a metal M in the modification α (stable modification).	Solution of a salt of the metal M.	Electrode of the metal M in the modification β (metastable modification).



Since, up to the present, no metal was known which, at suitable temperatures, occurs in two modifications, it was impossible to realise an element of this kind. As Dr. VAN EYK and I have shown [1]), the metal tin has a transition point at 20° C. Below this temperature the socalled grey tin is the stable form, above it the white.

Since the white modification may be considerably supercooled we may put together, below 20° C, an element (see Fig.) of the form

[1]) Report of the session of June 24th, 1899, p. 36, and of this session, p. 149.