

*Citation:*

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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.

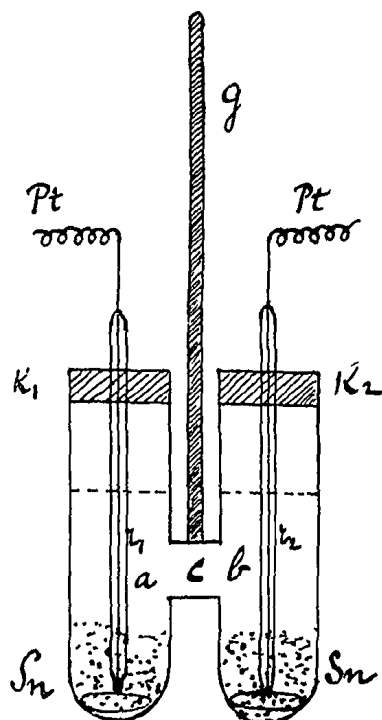
*Amsterdam*, Chemical Laboratory of the University,  
September 1899.

**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 $\alpha$ (stable modification).	Solution of a salt of the metal $M$ .	Electrode of the metal $M$ in the modification $\beta$ (metastable modification).
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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<sup>1)</sup>, the metal tin has a transition point at 20° C. Below this temperature the so-called 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

<sup>1)</sup> Report of the session of June 24th, 1899, p. 36, and of this session, p. 149.

Electrode of grey tin.	Solution of a tin salt.	Electrode of white tin.
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In the figure, *a* and *b* are glass tubes, 7 cm. long and 1½ cm. wide united by the wide middle-piece *c*.

The grey modification of the tin is placed in *a*, the white in *b*. In contact with the powder in each tube is a platinum wire, *r*<sub>1</sub> and *r*<sub>2</sub>, which is fused into a glass tube and bent into a ring at its lower end. An electrode made in this way has many advantages in practice <sup>1)</sup>.

An aqueous solution of a tin salt is poured into *a*, *b* and *c*, and *a* and *b* are closed with corks, *k*<sub>1</sub> and *k*<sub>2</sub>, which allow the wires *r*<sub>1</sub> and *r*<sub>2</sub> to pass. The whole element thus formed may be suspended in a thermostat by means of the glass rod *g* which is fused to it.

2. The theory of this element is easily given and offers, as will appear, many points of interest.

If an electrode of grey tin is placed in a dilute solution of a tin salt, in which the tin ions have an osmotic pressure *p*<sub>1</sub>, the potential difference between the electrode and the solution at the temperature *T* is

$$E_1 = \frac{RT}{n \epsilon_0} \log. \frac{P_g}{p_1} ,$$

where *n* is the valency of the tin,  $\epsilon_0$  the number of coulombs attached to 1 gramion, *P*<sub>g</sub> the electrolytic solution tension of the grey tin at the temperature *T* and *R* the gas constant.

If an electrode of white tin is now placed in the same solution we obtain

$$E_2 = \frac{RT}{n \epsilon_0} \log. \frac{P_w}{p_1} .$$

The E. M. F. of the transition element so obtained is then represented by the equation

$$E = E_1 - E_2 = \frac{RT}{n \epsilon_0} \log. \frac{P_g}{P_w} \text{ Volt} = \frac{0.0001983}{n} \log_{10} \frac{P_g}{P_w} \text{ Volts. . (I)}$$

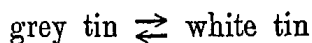
Since  $\frac{0,0001983 T}{n}$  is a constant at a given temperature we see

<sup>1)</sup> See RICHARDS and LEWIS, Zeitschr. für phys. Chemie, Bd. 28, S. 1 (1899).

from this that the E. M. F. of the element is simply a function of the electrolytic solution tensions of the two modifications of tin.

The employment of the element described as a transition element depends on the fact that at the transition temperature the two modifications become identical, the grey modification being transformed into the white. In equation (I),  $P_g$  and  $P_w$  are then equal and  $E = 0$ .

In order to discover the transition point of the change



it is therefore only necessary to find the temperature at which  $E = 0$ . The application of this method is to be found in the communication which Dr. VAN EYK and I made some time ago on the Enantiotropy of tin <sup>1)</sup>.

We can now go a step further and investigate the electrolytic solution tensions. We require the equations

$$E_1 = \frac{RT}{n \epsilon_0} \log. \frac{P_g}{p_1} \quad \text{and} \quad E_2 = \frac{RT}{n \epsilon_0} \log. \frac{P_w}{p_1} .$$

By placing an electrode of grey or of white tin in a dilute solution of a tin salt and combining it with a normal (Hg—HgCl— $\frac{1}{10}$ N . KCl) electrode,  $E_1$  and  $E_2$  may be separately determined. If the dissociation of the tin solution is known, all the quantities required to calculate  $P_g$  and  $P_w$  are then known.

From the equations we obtain

$$P_g = p_1 \cdot 10^{\frac{n E_1}{0.0001983T}} \quad \text{and} \quad P_w = p_1 \cdot 10^{\frac{n E_2}{0.0001983T}}$$

4. In the first place an element was prepared with a sample of grey tin from Prof. HJELT of Helsingfors and the ratio  $\frac{P_w}{P_g}$  determined at different temperatures.

Recently we have succeeded in converting ordinary Banca tin into the grey modification in any desired quantity <sup>2)</sup>. The measurements here described are to be repeated with this material which is particularly pure and the results together with the details of manipulation will be described in a later communication.

<sup>1)</sup> See note 1 on pag. 149

<sup>2)</sup> See pag. 152.

Temperature.	Ratio $\frac{P_w}{P_g}$
5°	1,067
10°	1,043
15°	1,017
20°	1,000

The ratio is calculated by means of the equation

$$\frac{P_g}{P_w} = 10^{\frac{n E'}{0.0001983 T}}$$

5. Below the transition temperature the modification which is metastable (the white) should have a greater solution tension than the grey ( $P_w > P_g$ ). From this it follows that grey tin must be precipitated from tin solutions below 20° C. when white tin is brought in contact with them, just as copper is precipitated from a copper solution into which a zinc rod, for example, is dipped.

The metal with the greater solution tension goes into solution whilst that with the smaller is precipitated.

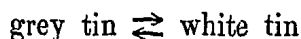
6. In our researches on the Enantiotropy of tin<sup>1)</sup> it was found that the conversion of white tin into the grey modification is highly favoured by the presence of traces of grey tin.

What has just been said about the solution tension of the two modifications explains the fact that the presence of a solution of a tin salt is also very favorable to the conversion of white tin into grey tin.

Below 20° C. grey tin is always precipitated from the solution of a tin salt by white tin; this process takes place, by analogy with what we know of other metals, very fast. In contrast to what so often happens with salt solutions, supersaturation does not occur.

If traces of grey tin are once present, they have a further accelerating action on the process. (According to experiment.)

7. We may now deduce another relationship which must exist between the displacement of the transition point of the reaction



with the external pressure exerted on the system and the temperature coefficients of our transition element.

For the grey tin electrode we have

<sup>1)</sup> See note on pag. 149.

$$E_1 = \frac{i_1}{n \epsilon_0} + T \frac{d E_1}{dT} \dots \dots \dots (1)$$

Here  $E_1$  is the difference of potential, at the absolute temperature  $T$ , between the grey tin and the tin solution in which it is immersed,  $i_1$  is the heat of ionisation of the grey tin,  $n$  the valency, and  $\epsilon_0 = 96540$  Coulombs.

For the white modification we have:

$$E_2 = \frac{i_1 + r}{n \epsilon_0} + T \frac{d E_2}{dT} \dots \dots \dots (2)$$

in which  $r$  represents the heat of transition.

From (1) and (2) we obtain, since  $E_1 = E_2$  at the transition temperature,

$$\frac{i_1}{n \epsilon_0} + T \frac{d E_1}{dT} = \frac{i_1 + r}{n \epsilon_0} + T \frac{d E_2}{dT}$$

of

$$r = n \epsilon_0 T \left( \frac{d E_1}{dT} - \frac{d E_2}{dT} \right) \dots \dots \dots (3)$$

Now we know that

$$T \frac{d D}{dT} = \frac{r_1}{V_w - V_g} \dots \dots \dots (4)$$

where  $T$  is the absolute transition temperature,  $D$  the external pressure,  $r_1$  the quantity of heat which is evolved when 1 kg. of white tin is converted into the grey modification, that is the heat of transition for 1 kg., and  $V_w$  and  $V_g$  are the volumes of 1 kg. of each modification in cubic metres. Since  $r$  in equation (3) relates to one gram atomic weight and  $r_1$  in (4) to 1 kilogram, we have

$r_1 = \frac{1000 r}{A}$ , where  $A$  is the atomic weight of the metal forming the electrode.

From (3) and (4)

$$\frac{d D}{dT} = \frac{1000}{A} \frac{n \epsilon_0 \left( \frac{d E_1}{dT} - \frac{d E_2}{dT} \right)}{V_w - V_g} \dots \dots \dots (5)$$

The quantity to the right of the sign of equality is now expressed in Volt-Coulombs, or ergs  $\times 10^7$ . If we wish to ascertain the change of the transition point produced by a change of pressure of 1 atmosphere, we may write (5) as follows:

$$\frac{dD}{dT} = \frac{n \epsilon_0 \left( \frac{dE_1}{dT} - \frac{dE_2}{dT} \right)}{101.4 A (V_w - V_g)}$$

or :

$$\frac{dT}{dD} = \frac{101.4 A (V_w - V_g)}{n \epsilon_0 \left( \frac{dE_1}{dT} - \frac{dE_2}{dT} \right)} = 0,00105 \frac{A (V_w - V_g)}{n \left( \frac{dE_1}{dT} - \frac{dE_2}{dT} \right)}$$

The advantage of this equation, which so far as I am aware is deduced here for the first time, is, from the practical point of view, that it is possible to determine the displacement of the transition temperature by external pressure by means of electrical measurements, if the specific gravities of the two modifications forming the electrodes have been determined.

For the electrical determinations of the temperature coefficients of the two electrodes of the transition element in the neighbourhood of the transition point quite small quantities of the electrode material (1 or 2 grams) suffice, whilst for calorimetric determinations, which in the nature of things are less accurate, considerable quantities are required.

The result of the measurements will be communicated as soon as the specific gravity of the grey tin has been determined in a completely satisfactory way.

*Amsterdam, Chem. Lab. of the University, September 1899.*

**Chemistry.** — Prof. H. W. BAKHUIS ROOZEBOOM in presenting the dissertation of Dr. D. J. HISSINK: "*On mixed Crystals of Sodium nitrate with Potassium nitrate and of Sodium nitrate with Silver nitrate*", makes the following communication with respect to it.

This research is a third contribution to our knowledge of the phenomena observed in the solidification of fused mixtures of two substances which form mixed crystals and in the transformation of the mixed crystals into another modification.

With respect to the system  $\text{KNO}_3 + \text{NaNO}_3$  the fact is mentioned that mixed crystals are formed on solidification; the limits within which these can exist are, however, so narrow that it did not appear to be worth while to investigate the exact connection between the phenomena.

The solidification of the system  $\text{NaNO}_3 + \text{AgNO}_3$  belongs to a type of which no example was known. The meltingpoint line rises continually from the meltingpoint of  $\text{AgNO}_3$  ( $208,6^\circ$ ) to that of  $\text{NaNO}_3$  ( $308^\circ$ ). It consists, however, of two branches, *AC* and *CB*,