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**Chemistry.** — “Answer to Prof. E. COHEN to his observations under the title of *Allotropy and Electromotive Equilibrium*”.<sup>1)</sup> By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of Feb. 27, 1914).

Mr. COHEN's attack under the title of “Allotropy and electromotive Equilibrium” induces me to make the following remarks.

Mr. COHEN seems to think it anything but correct that I have ventured to enter a field of work, which had been proclaimed his territory of research in more than one address, treatise, and magazine.

This deed, however unpardonable it may appear in Mr. COHEN's eyes, may be very reasonably accounted for. If I had not seen a chance to throw new light on the phenomenon of allotropy, I should certainly not have occupied myself with it, as it would not have prompted me so urgently to investigation then, but when a few years ago I came to the conviction that the phenomenon of *enantiotropy* and *monotropy* and the allied phenomena might be united under a new point of view, by the assumption that every phase of an allotropic substance is built up of different kinds of molecules, I did not hesitate for a moment, but immediately set about to test the drawn up theory with my pupils. This is the reason that of late years I have studied the phenomenon of allotropy, and I do not think that there is anything in the line of conduct followed by me that can in the least rouse astonishment.

Further Mr. COHEN considers it necessary to point out that the form of my publications might give rise to misunderstanding, which would appear from a passage occurring in my latest paper<sup>1)</sup>, running: “In connection with the foregoing it is desirable to draw attention to this that according to these considerations the contact with the solution of a salt of the metal must have an accelerating influence on the setting in of the internal equilibrium of the metal.”

Mr. COHEN has taken offence at this sentence, because according to him I should have forgotten to mention that already fifteen years ago this fact was found by him and VAN EYK, and has since been explained by him.

This remark of Mr. COHEN is *very significant*, for I do not think that he could have made it apparent in a clearer manner that the contents of my communication “The application of the theory of allotropy to electromotive equilibria” have remained *perfectly* dark to him.

<sup>1)</sup> These Proc. XVI p. 708.

Messrs. COHEN and VAN EYK <sup>1)</sup> found that when e. g. white tin is left in contact with a tin solution at a temperature lying under the transition point, the conversion of the metastable white to the stable grey tin is accelerated. Mr. COHEN's explanation is this <sup>2)</sup> that when once a trace of grey tin is present, the tin from the solution will deposit in the grey modification on the grey tin, in consequence of the difference in "Lösungstension" of white tin and grey tin, the white tin entering the solution. It is clear that all this refers to the conversion of one modification to another or of one solid phase to another.

My paper does not deal with the transformation which takes place between two solid phases of an allotropic substance, but with *the chemical conversion which can occur between the different kinds of molecules in each of the solid phases according to the theory of allotropy.*

In the cited communication I namely pointed out that the just-mentioned theory states that a metal which presents the phenomenon of allotropy, will contain different kinds of molecules. To simplify the case as much as possible I assumed that double molecules  $M_2$  occur by the side of simple molecules  $M$ . If the metal is now to behave as a substance of one component, so in a unary way, it is necessary that the different kinds of molecules in each of the phases of the metal are in equilibrium, and as we have to do here with an equilibrium between the kinds of molecules of one and the same substance, the word "internal equilibrium" is used here to distinguish it from other equilibria.

Up to now it has always been assumed that a metal emits only one kind of ions into solution. In connection with the just-mentioned internal equilibrium in the homogeneous metal phase we come, however, to the conclusion that the metal supposed here immersed in an electrolyte will emit different ions, which, if the ion per atom carries e. g. three positive charges, will be the ions  $M^{+++}$  and  $M_2^{+++}$ .

Just as the molecules  $M$  and  $M_2$  in the homogeneous metal phase can be in equilibrium, this will also be the case for the ions  $M^{+++}$  and  $M_2^{+++}$ , and this equilibrium, too, may be called an internal equilibrium.

Now I have among others pointed out that the metal can be in unary electromotive equilibrium only when the different kinds of

<sup>1)</sup> Zeitschr. f. phys. Chem. 30, 601 (1899).

<sup>2)</sup> " " " " 30, 623 (1899).

molecules in the metal and the different kinds of ions in the electrolyte each in itself, are in internal equilibrium.

It is to be expected that at the ordinary temperature the internal metal ion equilibrium sets in rapidly, whereas the metal in itself at the ordinary temperature does not pass into the state of internal equilibrium, or only exceedingly slowly.

When, however, the metal is brought into contact with an electrolyte which contains the ions of this metal, the surface of the metal, as I have demonstrated, will assume internal equilibrium in consequence of this that more of those ions in which the metal is deficient, deposit as molecule from the electrolyte, or that the metal sends more of those molecules as ion into solution which have too great a concentration in the metal. These two processes, which dependent on the concentration of the metal can also proceed simultaneously, bring about that the concentration of the surface of the metal becomes equal to that which corresponds to the internal metal equilibrium at the given temperature and pressure. In the maintaining of this equilibrium between the molecules  $M$  and  $M_2$ , as well as in its setting in, the electrolyte as connective link, will play an important part.

So, it appears convincingly from what precedes, just as from my previous communication, that the quoted passage refers to the transformations which take place when a metal phase which is not in internal equilibrium, passes into the state of equilibrium.

Also where I mention the transition point, I have said: "At the point of transition the electrolyte will greatly promote the internal equilibrium both in the metal  $e$ , and in the metal phase  $d$  for the just-mentioned reasons."

The case referred to by Mr. COHEN, the influence of an electrolyte on the conversion of one modification to another, I have therefore left entirely *out of consideration*, and as it is not exactly practical to mention the names of those who have occupied themselves with other phenomena, there was no occasion for me to mention Mr. COHEN in my preceding paper.

This *will*, however, be the case when I shall discuss also the influence which Mr. COHEN has in view, when it will appear that a deeper insight is attained just by means of the considerations given in my preceding communication.

In conclusion in reference to the motive of Mr. COHEN's attack, which according to him is to be found in the fact that more and more both Dutch and foreign colleagues should have objected to the line of conduct followed by me, I will only remark that different Dutch colleagues have expressed their sympathy with my work to

me. And as Mr. COHEN also mentions foreign countries, I may add that I have, indeed, carried on a controversy with Mr. TAMMANN, from which it therefore appears that on that side, as I had, indeed, expected, I meet with opposition; but I may state that on the other hand both before and after this controversy I have received expressions of great sympathy with my views from very competent colleagues from Germany, Sweden, England, and America, expressed in letters or publications, which if this should be considered desirable, I shall be glad to lay before the Committee of this Academy.

*Amsterdam, Febr. 1914.*

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(April 23, 1914.)