Chemistry. — *"The Phenomenon Electrical Supertension"*. II. By
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In the first communication on the phenomenon of electrical super-
tension the supertension of the hydrogen etc. has been considered
which appears at unattackable electrodes on the passage of an
electric current. Now we shall discuss the phenomenon of super-
tension at the generation of hydrogen, which occurs when metals
act on water, or on solutions of acids without the aid of an electric
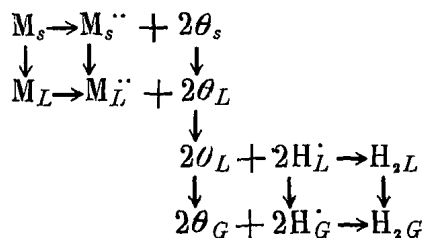current, i.e. *without entrance of electrons from outside.*

In the discussion of the hydrogen generation on immersion of
zinc in an acid zinc salt solution the adjoined figure 1 led us to
make the following remarks.

When zinc $(M^{\cdot\cdot})$ is placed in a liquid of the concentration x_1,
the zinc can be electromotively in equilibrium with this solution,
but only metastable, at an electrical potential indicated by the dotted
line gf.

In this case no hydrogen-generation should, however, take place.

The metal zinc does act, however, on the here supposed liquid,
and hydrogen is generated, which gives rise to a *three-phase equili-
brium*, consisting of a hydrogen-containing metal phase, a hydrogen
phase, and the electrolyte, in which we should bear in mind that
by what is here indicated as electrolyte, the liquid phase in the
boundary layer is meant. On action of the metal on the electrolyte
the concentration of the liquid in the boundary layer will differ
from that of the liquid outside the boundary layer.

In consequence of the reactions

$$\begin{array}{ccc} M_s \rightarrow & M_s^{\cdot\cdot} & + 2\theta_s \\ \downarrow & \downarrow & \downarrow \\ M_L \rightarrow & M_L^{\cdot\cdot} & + 2\theta_L \\ & \downarrow & \\ & 2\theta_L + 2H_L^{\cdot} \rightarrow H_{2L} \\ & \downarrow \quad \downarrow \quad \downarrow \\ & 2\theta_G + 2H_G^{\cdot} \rightarrow H_{2G} \end{array}$$

the liquid in the boundary layer will be poorer in hydrogen-ions
and richer in zinc-ions than the electrolyte outside the boundary
layer.

When now also on rapid solution the metal assumes internal equilibrium superficially, the metal phase will lie on ad or on the
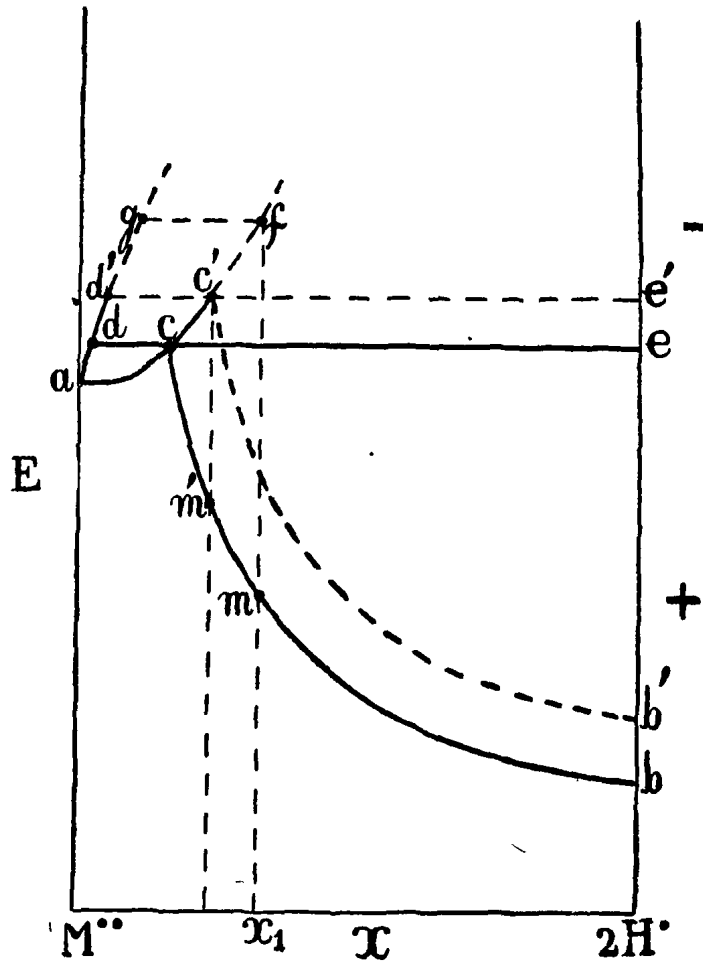

$\mathcal{F}ig$ 1

prolongation of this line, because the different points of this curve and its prolongation represent states of internal equilibrium of the metal in electromotive equilibrium with electrolytes which lie on the line ac or its prolongation.

When not only the metal phase, but also the hydrogen phase of the three-phase equilibrium mentioned just now is in internal equilibrium, the metal phase must lie in d, the hydrogen phase in e, and the electrolyte in the boundary layer in c, the electrolyte outside the boundary layer possessing the concentration x_1. The zinc-ions will, therefore, continually diffuse from the boundary layer outwards,

and the hydrogen ions in opposite direction from outside into the boundary layer.

Let us now first of all suppose that the internal equilibrium in the metal sets in very rapidly, but not in the hydrogen. This may take place when the metal maintains its internal equilibrium also on rapid emission of ions and electrons, and the internal equilibrium:

$$2\theta + 2H \cdot \rightleftarrows H_2$$
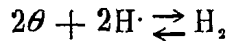
does not set in rapidly enough, so that a gas-phase escapes which contains too many electrically charged particles, i.e. too many ions and electrons or in other words is disturbed in *base direction*. In this case the three-phase equilibrium: metal phase – boundary liquid – hydrogen phase will be indicated by e. g. the three points $d'c'e'$.

When the electrical potential of the same disturbed hydrogen phase could be measured with regard to the electrolytes of other hydrogen-ion concentrations than c', the line $b'c'$ would denote the electrolytes which can coexist with the same disturbed hydrogen for different electrical potentials.

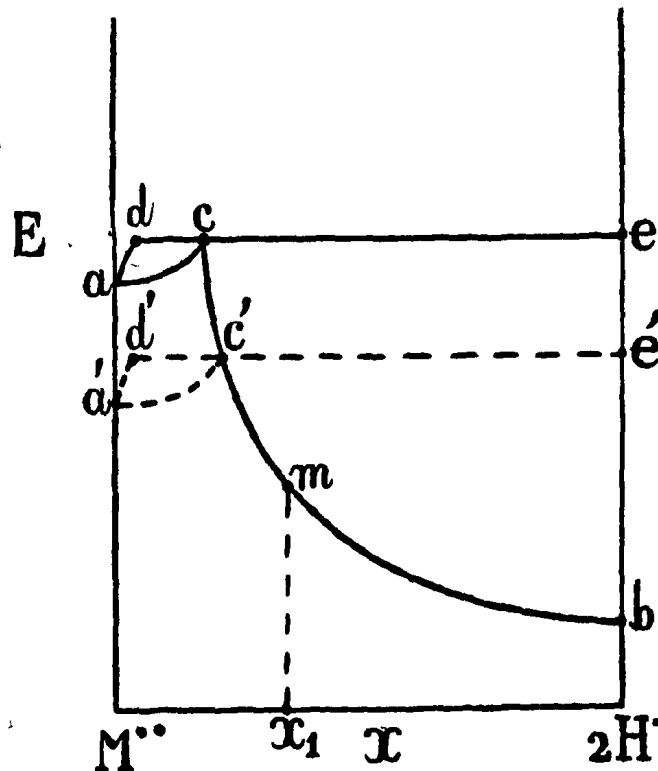We shall now consider the case that the internal equilibrium sets

Fig 2

in very rapidly for the hydrogen, but that the metal is disturbed. It being supposed here that the metal dissolves pretty rapidly, the liquid in the boundary layer will deviate also here from that outside the boundary layer with the concentration x_1. The hydrogen phase is in internal equilibrium, so that the coexisting liquid must be a point of the line bc. The disturbed metal phase is ennobled, and has, therefore, a less negative electrical potential. Let this metal phase be indicated by d', then the three coexisting phases are represented by the points $d'c'e'$, and the line $a'c'$ has only significance for the case that the same disturbed metal phase could also coexist with other electrolytes than c'.

A third possibility remains, namely this that neither the metal phase nor the gas phase assume internal equilibrium with sufficient rapidity. In this case the metal will, therefore, contain too few ions and electrons, in consequence of which its electrical potential has become less ·negative, whereas the hydrogen phase contains too many ions and electrons, from which results that its potential has obtained a more negative value.
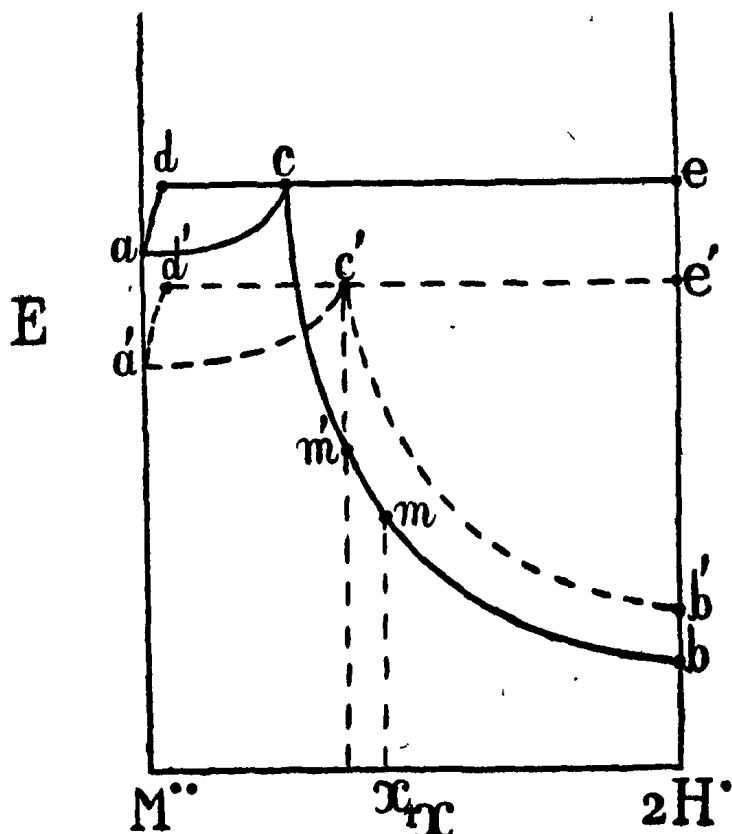

$\mathscr{Fig}$. 3

In this case the metal has, accordingly, become *ennobled*, but the hydrogen has become *baser*.

It is now the question at what potential the three-phase equilibrium will lie.

When the disturbance of the metal is much greater than that of the hydrogen, the three-phase potential will most probably be less negative than in case of internal equilibrium of metal and hydrogen phase; if, however, the disturbance of the hydrogen is very great, it is possible that this disturbance prevails, and that the three-phase potential 'is more negative than in case of internal equilibrium. In the foregoing diagram, fig. 3, the former is supposed.

It is clear how on these considerations we are gradually led to the case that presents itself for Nickel.

There the metal is disturbed, and through its exceedingly slow, imperceptible generation the hydrogen is always in internal equili-

Fig. 4
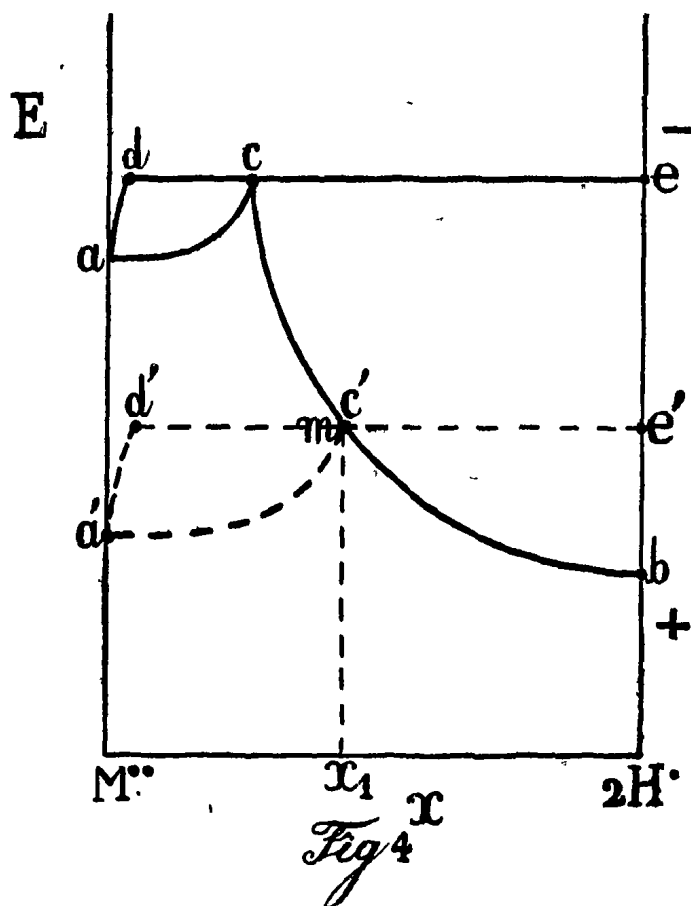
brium. In consequence of the exceedingly slight action the concentration of the boundary liquid is practically not different from that outside the boundary layer, so that the liquid phase of the three-

phase equilibrium will be indicated by the point m, so that the three-phase potential coincides with the potential of the hydrogen electrode, as was already demonstrated before.

Now it is perfectly clear from the considerations given here that we are not justified in saying that when the hydrogen generates at a metal of a potential which is baser than that of the hydrogen electrode, the hydrogen presents the phenomenon of supertension. Fig. 2 e.g. refers to this case, here the generated hydrogen shows no supertension, because the liquid lies in the boundary layer on the line bc. The point c' lies, indeed, above m, but this is only owing to this that in consequence of the solution of the metal, the concentration of the liquid, in the boundary layer, is different from that outside it.

In the cases represented by figures 1 and 3 the hydrogen presents supertension, but this supertension is not equal to the potential difference between the potential of the generating hydrogen and the hydrogen electrode, for in order to get to know the supertension it would be necessary to have the hydrogen electrode also in the boundary layer of the dissolving metal.

The real supertension can be read from the figures 1 and 3 mentioned, it is not the distance from the point m to the horizontal line $d'e'$, but equal to the distance $m'c'$.

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