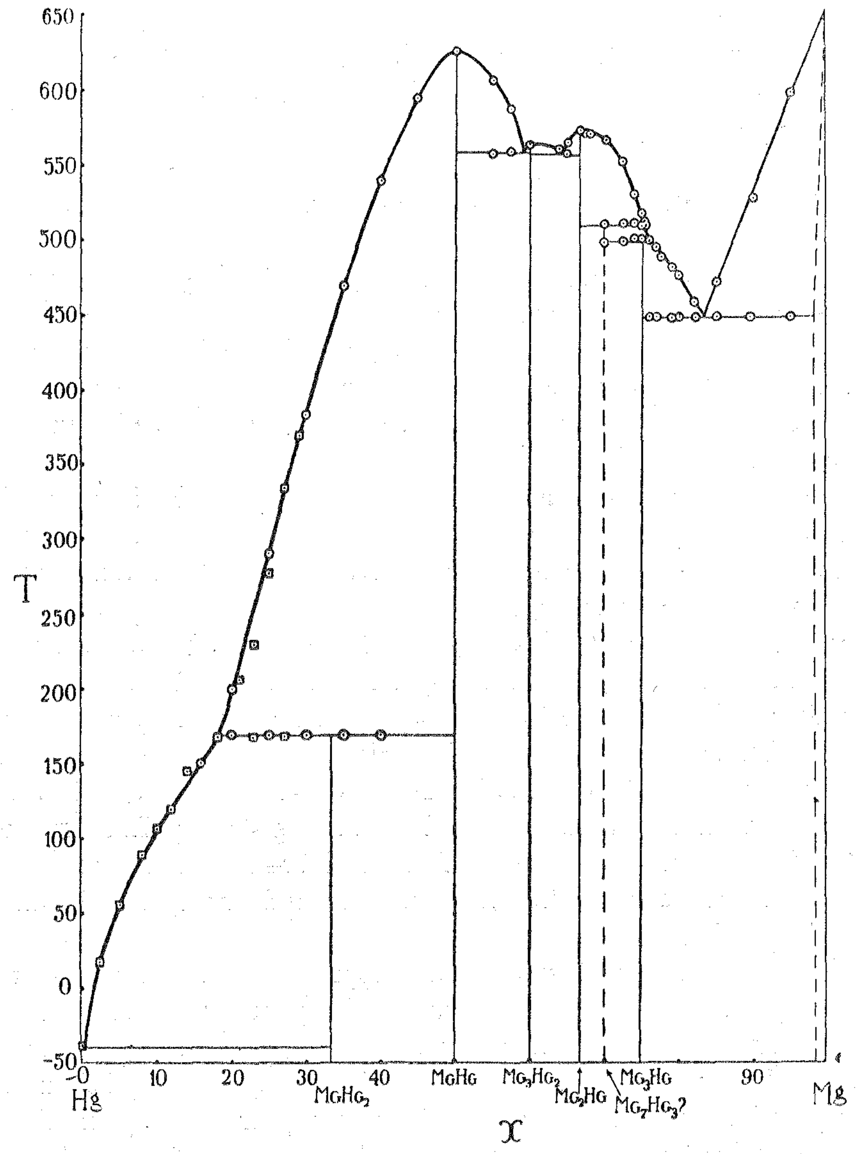
After the T,X-diagram found had given something of a general insight, the investigation of the electromotive behaviour of Mg—Hg-



mixtures was started, the results of which will be communicated in a following publication.

Laboratory of General and Inorganic Chemistry of the University.

Amsterdam, December 13 1920.

Chemistry. — *"A Thermo-electrical Differential Method for the Determination of Transition Points of Metals at Comparatively Low Temperatures"*. By Prof. A. SMITS and J. SPUYMAN. (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of December 18, 1920).

This paper should be considered as a continuation of the publication "The Thermo-electrical Determination of Transition Points I" [1]). In the latter paper it was already stated that the very favourable results obtained by us on application of the thermo-electrical method in the investigation of the combination, iron-tin, and copper-tin, induced us to examine also other important metals in the same way, starting with copper. Our purpose was to examine in the first place whether copper shows a point of transition in the neighbourhood of 70°. The arrangement which we used at first for this purpose is represented in outline in the subjoined figure.

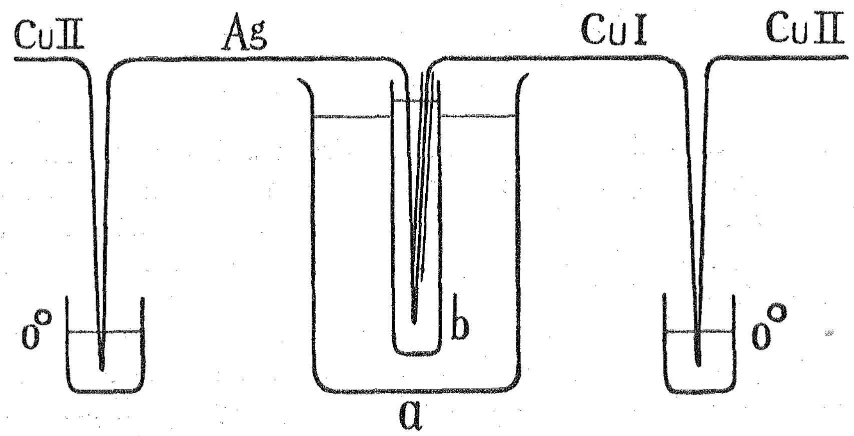


Fig. 1.

The combination pure silver-pure copper (Cu I), of which the copper wire is passed through a glass capillary, was placed in a wider tube b, filled with an electrolyte, with which silver and copper were in electromotive equilibrium. For this purpose we took a solution of copper-sulphate, because the electrolyte, which is in

[1]) These Proc. Vol. XXIII, 5, p. 687.

electromotive equilibrium with copper and silver, contains but exceedingly little silver.

As was shown before [1]) there then exists between the copper and the silver wire still a potential difference equal to the Volta-effect. Now the tube *b* was placed in a thermostat *a* and the two soldering places Ag—Cu II and Cu I—Cu II in melting ice. After the thermostat had been kept constant at a definite temperature for some time, the electromotive force of the circuit was measured. This measurement, ranging over a temperature interval of from 40°—80°, gave no indications of a discontinuity in the neighbourhood of 60°, after which it was resolved to apply a more accurate measurement, which we found in a method, which we shall call the *differential method*. The arrangement of this differential method is given in outline below in Fig. 2.

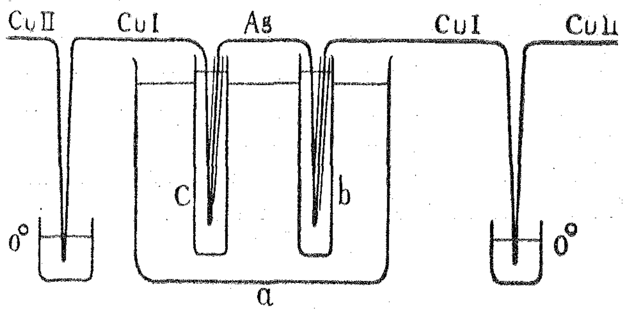


Fig. 2.

The two extremities of the silver wire, which are soldered to wires of pure copper, are now *both* in the thermostat *a*, but the capillary *b* is filled with a solution of copper sulphate, and *c* contains anhydrous paraffin oil. Both solutions are under a nitrogen atmosphere [2]).

The consideration that led to this arrangement, is as follows. So long as no transition point is reached on change of temperature, the electromotive force of the circuit will be very small, hence it will change but exceedingly little with the temperature in the thermostat; but when a transition temperature of silver or copper is passed, it is probable that the thread of the *differential thermoelement*, which is in electromotive equilibrium with the electrolyte, is

[1]) These Proc. Vol. XXI, 3, p. 386.

[2]) In reality the tubes *b* and *c*, which contain the metal wires immersed in a liquid, have been first exhausted of air, then filled with nitrogen, and finally fused to.

sooner transformed than the thread of the same combination which is immersed in paraffin oil [1]).

If this is actually the case, the electromotive force of the differential thermo-element will undergo a rather sudden change, and the initial point of this change will correspond with the transition point of one of the metals of the element. On application of this simple and very sensitive differential method it was found that the electromotive force was practically zero throughout the temperature range that we examined, for it was less than 0,001 milli Volt. We did not consider the investigation as finished then, and we once more examined the same differential thermo-element Cu—Ag—Cu, taking care that one pair of wires was not only immersed in a solution of $CuSO_4$, but in such a way that the etched copper wire, the soldering place, and a small piece of the silver wire were in contact with powdery copper.

This procedure in our experiment, however, did not bring about the slightest change in the results, for now too the electromotive force of the circuit between 40° and 80° remained certainly smaller than 0,001 milli-Volt.

We will still mention here that the times of observation have been taken very long here on purpose, and amount to 2×24 hours. Notwithstanding this prolonged heating at temperatures above and below those at which dilatometrically indications were found for a transition point, the electromotive force of the differential thermo-element appeared to be smaller than 0,001 milli-Volt. In the first place this result shows that both the silver wire and the copper wire were very homogeneous, and in the second place that neither the silver wire nor the etched copper wire, though they were in contact with a solution of $CuSO_4$ and with fine copper powder over a length of 20 cm., showed appreciable transformation.

The differential method discussed here is now being applied to the other important metals. In the following paper also the theory will be discussed.

Laboratory of General and Inorganic Chemistry of the University.

Amsterdam, December 13, 1920.

[1]) For COHEN found that contact with an electrolyte has an accelerating effect on the transformation of one metal modification into another. This accelerating action must probably be ascribed to this, that when the stable modification has appeared only in one point, this gives rise to local currents, which greatly promote the transformation.