here, which extends in the saturate solution up to 0,231 gr. mol. per liter and in the mixed crystal phase up to 1.947 gr. mol. per liter, is really a constant quantity. With greater concentrations the quotient $\frac{C_L}{C_S}$ presents a course as was also to be expected; the quotient then becomes smaller, as the latter value indicates.

Now that this result had been obtained, it was of course supposed that also on the dichlorine side the law of partition would prove valid. Mr. MEYER's investigation yielded results in concordance with this expectation, which are recorded in Table II. (see p. 685).

Here too only the quotient $\frac{C_L}{C_S}$ yields values that vary only within the errors of analysis over a definite range of concentration, viz. up to a dibromine concentration in the solution of 0,04 gr. mol. and in the mixed crystal of 0.72 gr. mol. Hence we may conclude that this quotient, which has of course another value than the corresponding quotient on the di-bromine side, is in reality a constant quantity.

The results given here are of great importance. They justify us in concluding that also for the diluted component in a diluted mixed crystal GIBBS's *paradox* will prove to be valid, and that we may, therefore, write for the equilibrium between a mixed crystal phase and a saturate solution:

$$RT \ln x_L + F(v . T)_L = v RT \ln x_S + Q(v . T)_S.$$

In a subsequent communication we shall see what conclusions may be drawn from the value of the factor v with regard to the molecular size of the diluted component in the mixed crystal phase.

Meanwhile Mr. MEYER is carrying on the investigation with other substances, among which also electrolytes.

Laboratory of general and inorganic Chemistry
of the University.

Amsterdam, May 28, 1920.

Chemistry. — *"The Thermo-electric Determination of Transition Points"*. I. By Prof. A. SMITS and J. SPUYMAN. Communicated by Prof. P. ZEEMAN.

In 1912 the transition point of tetrogonal tin into rhombic tin was determined by means of very lengthy and laborious determinations. Small quantities of mercury accelerated this transformation, but at the same time brought about a lowering of the transition point. Through extrapolation up to the quantity of mercury $= 0$ $200°.5$ was found as transition temperature, the subsequent experiments with pure tin, which gave a great deal of difficulty, yielding $\pm 202°.8$ in the end.[1]) Though it has appeared that also in other cases mercury is a catalyst for the transition from one metal modification to another, so that this expedient may often be successfully applied, it seemed very desirable to try and find another reliable and quicker method.

That thermo-elements can only be used over a range of temperature, within which no points of transition of the metals used occur, is known, and likewise the conclusion of the existence of a transition point was drawn before from a discontinuity of the change of the electomotive force with the temperature.

Thus among others in the examination of the thermo-elements Nickel-Copper[2]) and Nickel-Lead[3]) a discontinuity was found between $350°$ and $360°$, which points to a transition point of Nickel, with which also the study of the magnetic and mechanic properties and also the investigation of the change of length carried out by JÄNECKE,[4]) is in agreement. Further BRIDGMAN[5]) investigated the thermo-electric force of thermo-elements under pressure; we may, accordingly, say that the thermo-element has been used already several times to discover a point of transition in one of the metals of the thermo-element.

That, however, on rational application the thermo-electric method

[1]) SMITS and DE LEEUW, These Proc. Vol. XV, p. 676.

[2]) HARRISON, Phil. mag. **3,** 192, 1902; WIENER Z. f. anorg. Chem. **83,** 310 (1913).

[3]) Proc. Roy. Soc. Edinburg, **8,** 182 (1872—1873).

[4]) Z. f. Electr. Chem. 9 (1919).

[5]) Proc. Amer. Acad. **53,** 269 (1918).

supplies us with a method pre-eminently fit to discover transition points in metals, both on account of its accuracy and quickness, this was not yet known.

This we found in the following research, which was undertaken with a purpose to discover the above-mentioned transition point also by a thermo-electric way. For this purpose we first examined what metal combined with tin promised a good result. For reasons which will further be set forth in the theoretical discussion of this method, *iron* was chosen as second metal.

The investigation of the electro-motive force of this element at different temperatures gave the following result:

IRON-TIN.

Temperature	E. F. in milli-Volts
139.8°	1.30
146.8°	1.31
172.4°	1.39
183.5°	1.46
196.6°	1.63
199.2°	1.69
204.0°	1.72
208.4°	1.74
212.6°	1.79

after sudden cooling	
180.0°	1.65
180.0°	1.59
180.0°	1.53
180.0°	1.46
180.0°	1.43
170.4°	1.38

When we represent this result graphically, we get fig. 1, from which we see that the transition point appears very clearly, and lies at 200°.2, which result is in perfect harmony with the extrapolated value which followed from the dilatometer-examination of

mercury-containing tin. What was also very clearly to be seen here was this that, when a temperature lying above the melting-point of tin, was rapidly lowered, the transformation failed to appear, and the metastable prolongation of the upper branch could be followed
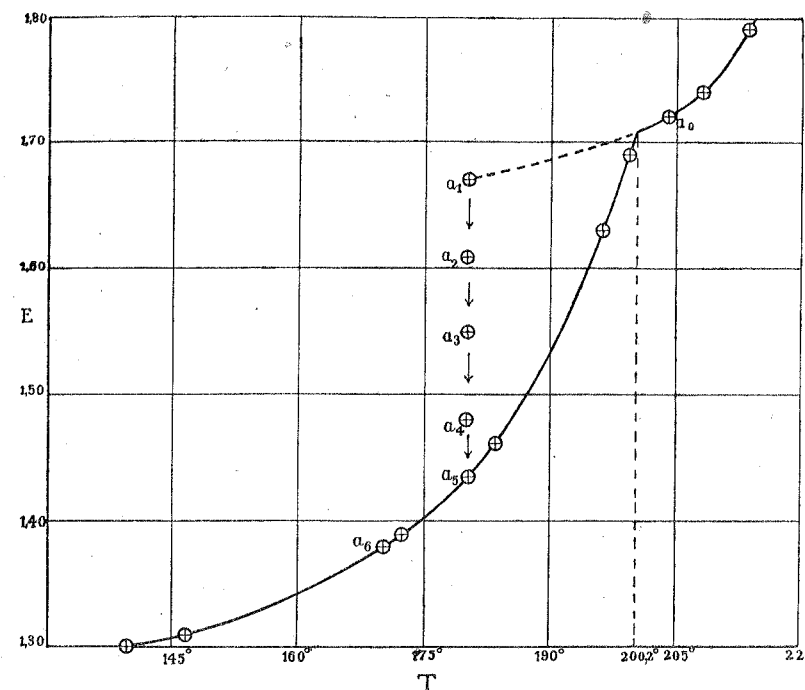

Fig. 1.

COPPER-TIN.

Temperature	E. F. in milli–Volts
158.0°	0.52
183.0°	0.63
198.0°	0.71
218.8°	0.79
210.0°	0.75
207.0°	0.74
191.0°	0.67
181.0°	0.62
153.0°	0.50
150.2°	0.49
202.0°	0.73

for some distance. If the temperature was then kept constant, the E. F. decreased till the stable branch was reached (see the points $a_0, a_1, a_2, a_3, a_4, a_5$).

In the second place tin was combined with copper, in which the following result was reached.

When these results are again represented graphically, the transition point of tin again makes its appearance at $200°.5$, in agreement with what precedes, but less clearly here. This is seen in fig. 2.
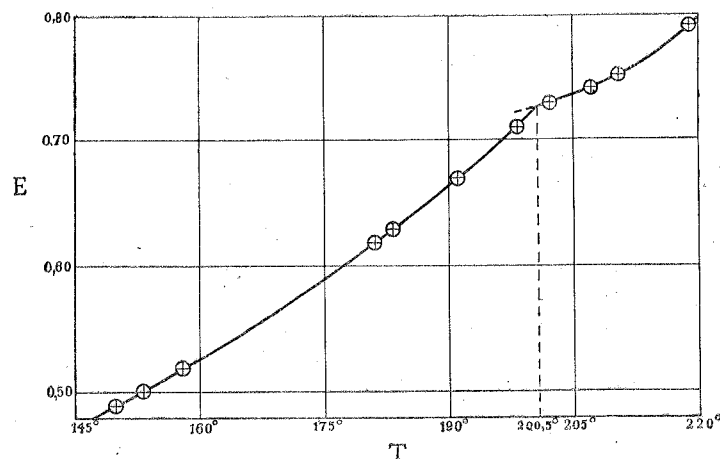

Fig. 2.

When in this way the reliability of this sensitive and rapid method had been proved, we applied it to ascertain whether in copper indications for a transition point could be observed in the neighbourhood of 70°. As is known, the dilatometric investigation [1]) gave no indication at all, no more than BRIDGMAN's researches.

The result of this investigation will be discussed in a following paper.

*Laboratory of general and inorganic chemistry of
the Amsterdam University.*

Amsterdam, May 23rd 1920.

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[1]) COHEN, These Proc. Vol. XVI, p. 628. (1914). Z. f. phys. Chem. **87**, 419 (1914).

Physics. *"Observations of the Temperature during Solidification"*. By Dr. H. C. BURGER. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of June 26, 1920).

1. When in a supercooled liquid in a cylindrical tube, a seed of the solid substance is inserted, the boundary plane of the solid substance moves with uniform velocity. This velocity (linear velocity of crystallisation) has been measured by many investigators as function of the temperature of the surroundings (thermostat), in which the tube is placed. They have, however, not measured the temperature prevailing during the solidification in the two phases and at their boundary plane, though it is the measurement of this temperature that is of great importance for the true insight into the process of solidification. More than once the opinion has been expressed that at the boundary plane solid-liquid the meltingpoint-temperature would prevail [1]), but no grounds were adduced in support of this statement. As, however, appears from my observations this is not the case, at least not for the substance examined by me.

The small quantity of substance, hence the small quantity of heat which is generated, renders it necessary that the instrument with which the temperature is measured, should have a very small heat capacity. If this is not the case, the distribution of the temperature in the substance is disturbed by the insertion of the instrument to such a degree that the temperature that is observed, is by no means equal to the temperature that would prevail at the same place, when this was absent. Besides the measurement of the temperature must take place with an instrument that possesses slight inertia, because the temperature that is measured at a fixed point of the tube, rapidly changes with the time. The temperature further should be registered, because reading is impossible on account of the rapid variation.

Consequently a temperature measurement must be chosen which is made by the aid of a thermo-element, which must have as small a mass as possible. The current supplied by this thermo-element in consequence of the rise of temperature in the tube, must be observed with a galvanometer, which is sufficiently rapid to follow the process

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[1]) W. HERGESELL, Ann. d. Phys. u. Chem., 15, 1882. p. 19.
G. TAMMANN, Kristallisieren und Schmelzen, 1903, p. 135.

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